PB-215 688

HYPOCHLORITE GENERATOR FOR TREATMENT OF COMBINED SEWER OVERFLOWS

Frank B. Leits, et al

Ionics, Incorporated

Prepared for:

Environmental Protection Agency

March 1972

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1 Accession Number	2 Subject Field & Group	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM
W	05D	

5 Organization

Ionics, Inc. Watertown, Massachusetts

6 Title

Hypochlorite Generator for Treatment of Combined Sewer Overflows

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16 Project Designation

EPA Program 11023 DAA & Grant 11023 DME

21 Note

Details of illustrations in this document may be better studied on microfiche

22 Citation

23 Descriptors (Starred First)

*Waste treatment, *water quality control, *water treatment, *Electrochemistry, Process Design, Brine, Chlorine, Computer Programs, Combined sewers

25 Identifiers (Starred First)

*Electrolytic hypochlorite generator, *Hypochlorite, Electrolytic Cell, Somerville, Massachusetts

27 Abstract

An advanced electrolytic generator has been developed for on-site production of sodium hypochlorite for disinfection of overflows from combined sewer systems. In this system an electrochemical cell electrolyzes sodium chloride brine to chlorine gas and sodium hydroxide solution, which are reacted immediately outside the cell to produce a 5 to 10% sodium hypochlorite solution. Significant advances in safety and economy have been realized by use of a hydraulically impermeable cation exchange membrane. The most critical components have operated for over 3000 hours with no deterioration of performance. The generator requires 1.6 KWH of electricity and 2.1 pounds of salt per pound of sodium hypochlorite. The operating cost for systems larger than 500 pounds of hypochlorite per day is projected to be 3 to 4 cents per pound of hypochlorite. ~~This cost~~ is significantly below that of truck-delivered hypochlorite solution. Such economy of operation should make the generator useful for a wide variety of water treatment applications. The first field unit is scheduled for installation at a Metropolitan District Commission facility, in Somerville, Massachusetts. (Leitz, Ionics)

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HYPOCHLORITE GENERATOR FOR TREATMENT OF COMBINED SEWER OVERFLOWS

by

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65 Grove Street
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for the

OFFICE OF RESEARCH AND MONITORING
ENVIRONMENTAL PROTECTION AGENCY

Program No. 11023 DAA
CONTRACT No. 14-12-490
and
GRANT No. 11023 DME
March, 1972

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 - Price $1.00

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ABSTRACT

An advanced electrolytic generator has been developed for on-site production of sodium hypochlorite for disinfection of overflows from combined sewer systems.

In this system an electrochemical cell electrolyzes sodium chloride brine to chlorine gas and sodium hydroxide solution, which are reacted immediately outside the cell to produce a 5 to 10% sodium hypochlorite solution. Significant advances in safety and economy have been realized by use of a hydraulically impermeable cation exchange membrane. The most critical components, the dimensionally stable anode and the ion-exchange membrane, have both operated for over 3000 hours with no deterioration of performance.

System operation has been given a first order economic optimization. At a current density of 240 ASF, the cell potential is 3.7 volts. The generator requires 1.6 KWH of electricity and 2.1 pounds of salt per pound of sodium hypochlorite. Salt utilization is over 80%. The operating cost for systems larger than 500 pounds of hypochlorite per day is projected to be 3 to 4 cents per pound of hypochlorite. This cost is significantly below that of truck delivered solution. Such economy of operation should make the generator useful for a wide variety of water treatment applications.

The first field unit is scheduled for installation in the Northeast Sanitary District in Somerville, Massachusetts, under Grant 11023 DME. The estimated operating and maintenance cost is estimated to be 3.7¢ per pound of chlorine or 0.13¢ per thousand gallons of overflow.

This report was submitted in fulfillment of Program No. 11023 DAA, Contract No. 14-12-490 and Grant 11023 DME under partial sponsorship of the Office Research and Monitoring, Environmental Protection Agency.

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CONCLUSIONS

1. On-site electrochemical generation of hypochlorite is an efficient, economical means of disinfecting combined sewer overflows. In most cases hypochlorite solution can be generated for considerably less than commercial prices for truck delivery.

2. A generator system has been developed, which consists of a brine saturator of conventional design, an electrochemical cell in which chlorine gas and sodium hydroxide solution are produced and a reactor in which these materials are reacted to produce sodium hypochlorite solution. The emphasis in the design has been on safety, reliability and unattended operation.

3. The principal components in the electrochemical cell are a DSA anode, a mild steel cathode and a fluorinated ion-exchange membrane separator, all of which have been satisfactorily life tested for over 3000 hours.

4. The most favorable configuration for an on-site cell is a two-compartment cell having a membrane separator and expanded metal electrodes adjacent to the membrane.

5. Hypochlorite cells have been run at high current densities, up to 500 ASF, without excessive loss in current efficiency or degradation of materials. The optimum current density depends upon various economic factors but generally is in the neighborhood of 250 ASF.

6. The major operating variables are catholyte concentration, current density and salt cut. A computer program, included in this report, was developed which predicts the optimum operating conditions for given values of salt and power cost and other economic parameters.

RECOMMENDATIONS

1. The laboratory modules have met or exceeded the performance specifications in the original design. Work should proceed on construction, installation and testing of the field unit, as scheduled.

2. Testing of the unit should include observation of component aging and measurement of performance with time under real intermittent operating conditions.

3. A study using modern methods of dynamic programming and incorporating hydrographic data from various regions in the country should be performed to develop the optimum policy with regard to production capacity of the unit, the fraction of time the unit should be designed to run, size of brine saturator and size of product storage tank.

4. Because of the variability of chlorine demand in outfalls during a storm or between storms, a means of controlling the dosage to the combined effluent should be developed.

5. A study should be made of the effects of calcium, magnesium and sulfate in the salt and in the feed water to determine what concentrations of these species in the brine can be tolerated. Several possible means of removal should be evaluated to determine which is most economical.

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SECTION I

INTRODUCTION

Many American cities possess combined storm and sanitary sewers. Interceptor sewers are usually sized to handle approximately 3 to 5 times the average dry weather flow. When a severe storm occurs, the combined sewer flow to the interceptor may increase to twenty to one hundred times the dry weather flow. Overflow weirs are generally located throughout a combined sewer system so that raw sewage is directed to treatment facilities during dry weather but, during wet weather, is directed to the local water course and will not back up into homes and streets under storm conditions. Installation of separate sewer systems in older cities is considered prohibitively expensive.

A minimum treatment of these overflows is brief retention and disinfection by addition of relatively small doses of chlorine gas or hypochlorite solution. Chlorine gas is highly toxic as well as corrosive. As a result of public concern regarding the dangerous nature of chlorine and the widespread news coverage of chlorine accidents, many cities are reluctant to use chlorine gas.

A safer alternative to use of chlorine gas is use of sodium hypochlorite solution. This is chemically identical to the bleach solutions used in most households. Advantages of the use of purchased hypochlorite are low capital cost and low maintenance since little equipment more than a storage tank and an automatic feed device is required. Disadvantages are that purchased solution is expensive, it requires truck delivery and the solution decomposes slowly but regularly which makes it undesirable to keep large quantities on hand.

In a study funded by the Environmental Protection Agency, a system was designed for on-site electrochemical generation of hypochlorite solution. This study, which was highly successful, resulted in the development of a system consisting of an electrochemical cell and a reactor, which produces a high quality solution of hypochlorite at prices which, for almost any reasonable commodity costs, are much lower than that of truck-delivered hypochlorite solution.

In this report the evolution and design of the system is described, results of life tests of components are presented, and operating, maintenance and capital costs are estimated. The first field test unit has been constructed for the Metropolitan District Commission of the Commonwealth of Massachusetts. Details of the application are discussed.

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SECTION II

DESIGN AND OPERATION OF HYPOCHLORINATOR

The major components of the hypochlorite generator are a stack of electrochemical cells and a caustic-chlorine reactor. In the cells sodium chloride is decomposed to chlorine and sodium hydroxide (caustic). Chlorine and caustic are combined in the reactor to produce sodium hypochlorite solution (hypochlorite). Figure 1 shows the assembled hypochlorite generator. A block flow diagram appears in Figure 2.

The electrochemical cell is the heart of the hypochlorite generator system. It consists of two electrode compartments separated by a membrane. Saturated brine is fed to the anode compartment. At the anode surface, chlorine gas is generated. The effluent from the anode compartment is sent to a gas-liquid separator where the chlorine gas is separated from the depleted brine, which is discarded. The membrane in the cell acts as a hydraulic barrier which permits electrochemical transport of sodium ions from the anode to the cathode compartment. A small quantity of water is fed to the cathode compartment. At the cathode hydrogen gas and hydroxyl ions are generated. The effluent from this compartment goes to a gas-liquid separator in which the hydrogen is removed from the caustic solution. The hydrogen is diluted with air to an innocuous level and vented to the atmosphere.

Chlorine and caustic are fed to the reactor with caustic in slight excess. The reactor is water cooled to avoid decomposition of hypochlorite and formation of oxygen. Insoluble gases, mainly oxygen, are removed in a gas-liquid separator before the hypochlorite is sent to the product storage tank.

Brine feed for the system comes from the salt storage tank, or lixator, which is used for both salt storage and production of saturated brine. The lixator is an item of commerce available in a variety of sizes, the choice of which depends upon the expected rate of salt usage. Generally, the lixator is obtained from the salt supplier. Because of the crystal properties of sodium chloride, the bed of salt acts as a filter for the saturated brine.

Since the hypochlorite is not used as it is produced, a storage tank is provided for it.

The basic components of the cell stack are the molded cell frame and the membrane package. The cell frame is shown by itself in Figure 3 and with electrodes installed in Figure 4. The membrane package appears on the right in Figure 4. The cell frame is injection molded from asbestos filled polypropylene with overall dimensions of 24" x 24-3/4" x 2". The cavity on one side of the frame forms the anode compartment

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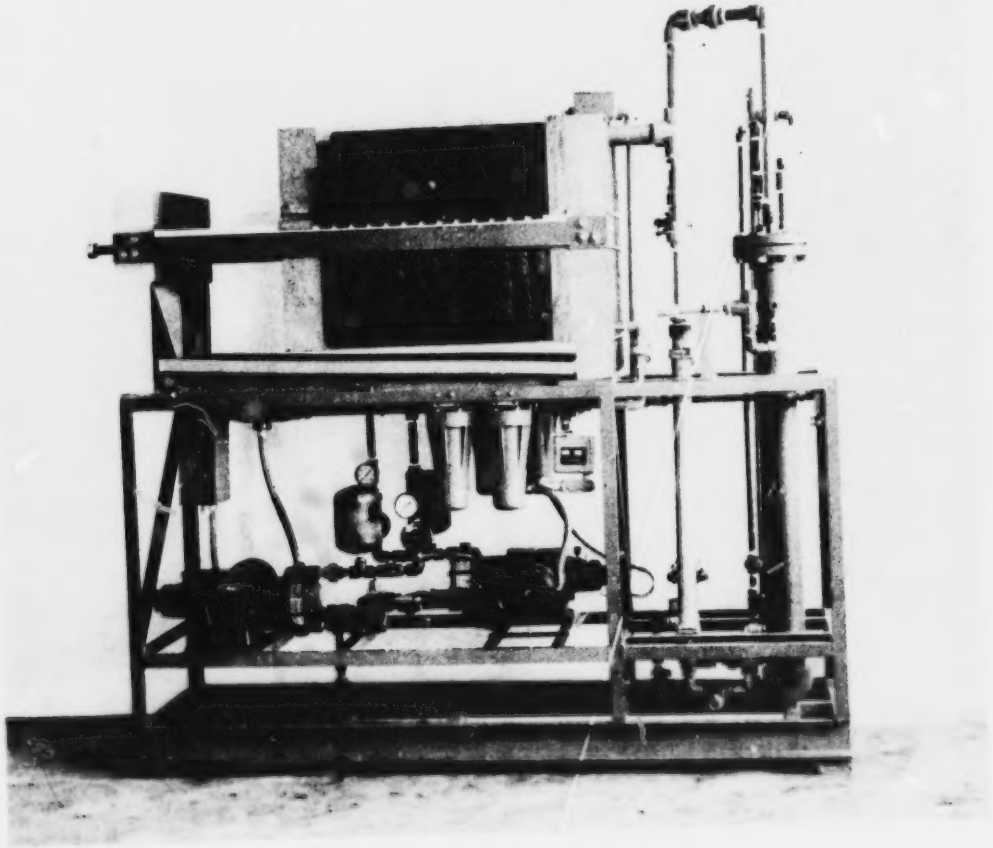

Figure 1. Electrochemical hypochlorite Generator

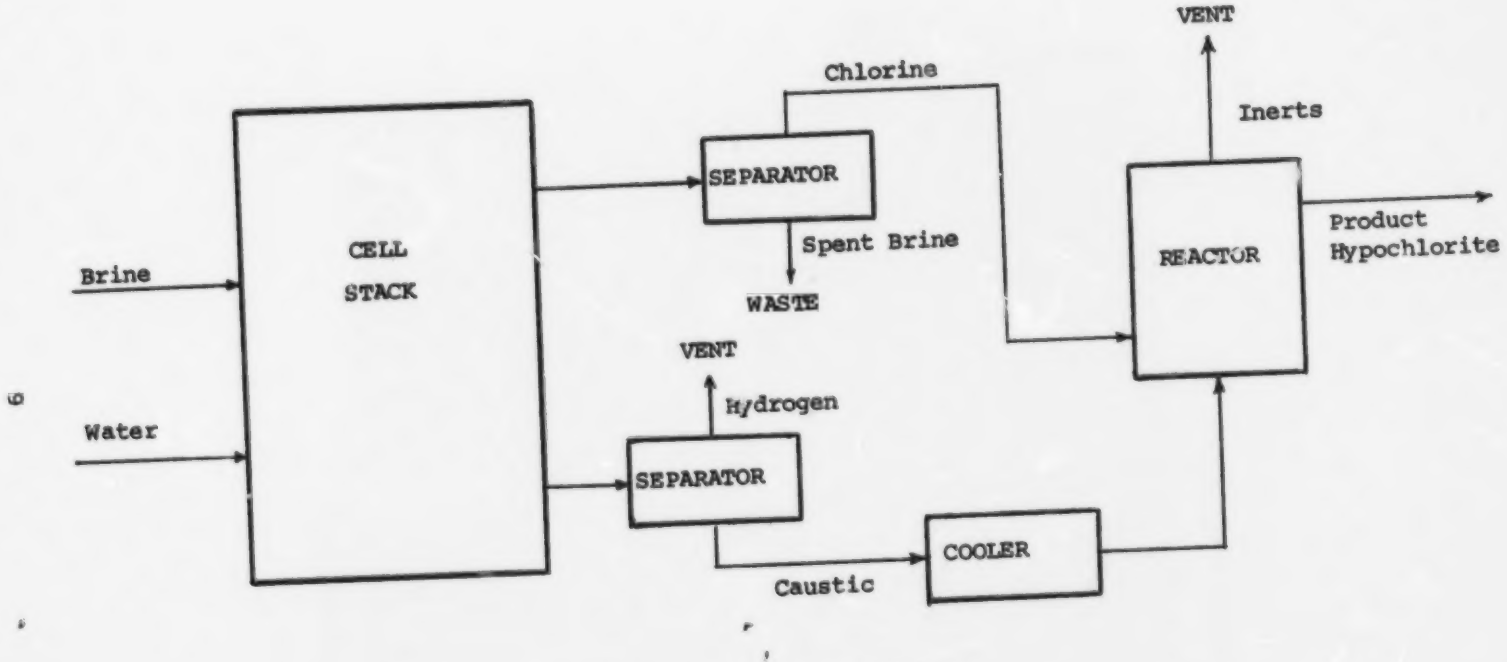

Figure 2. Hypochlorite Generator Block Flow Diagram

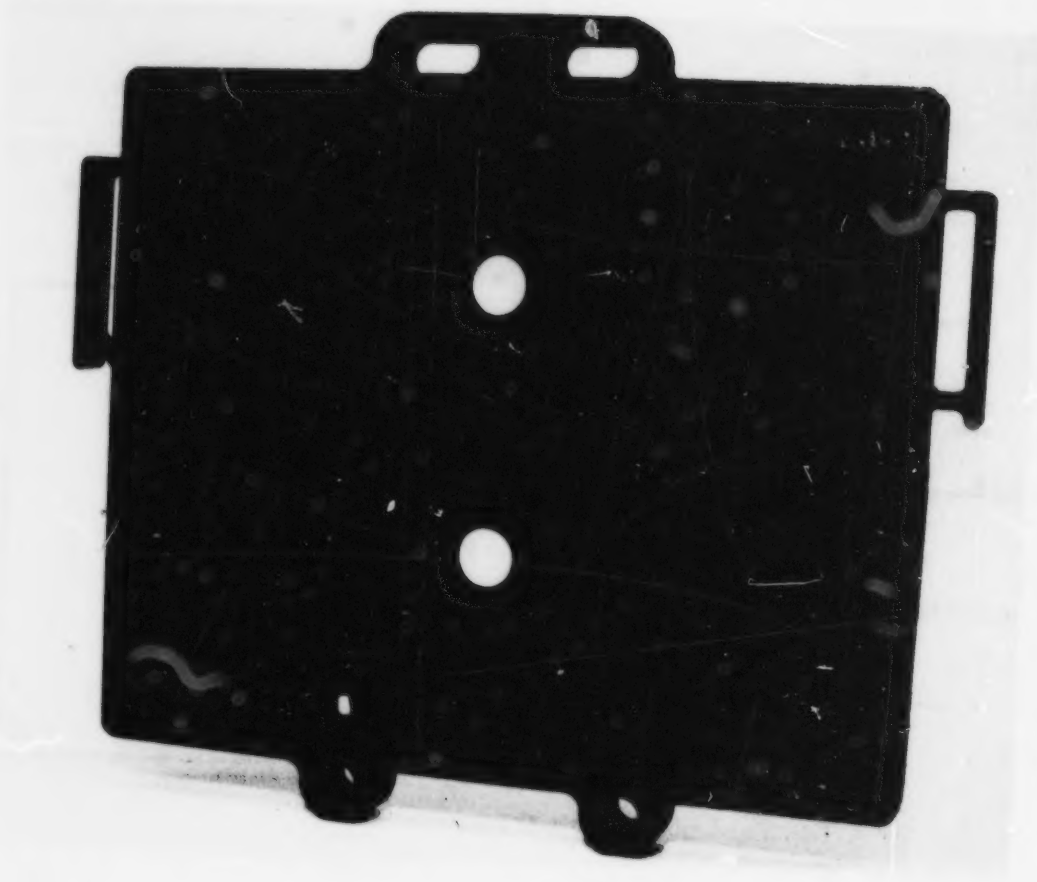

Figure 3. Molded C[illegible] Frame

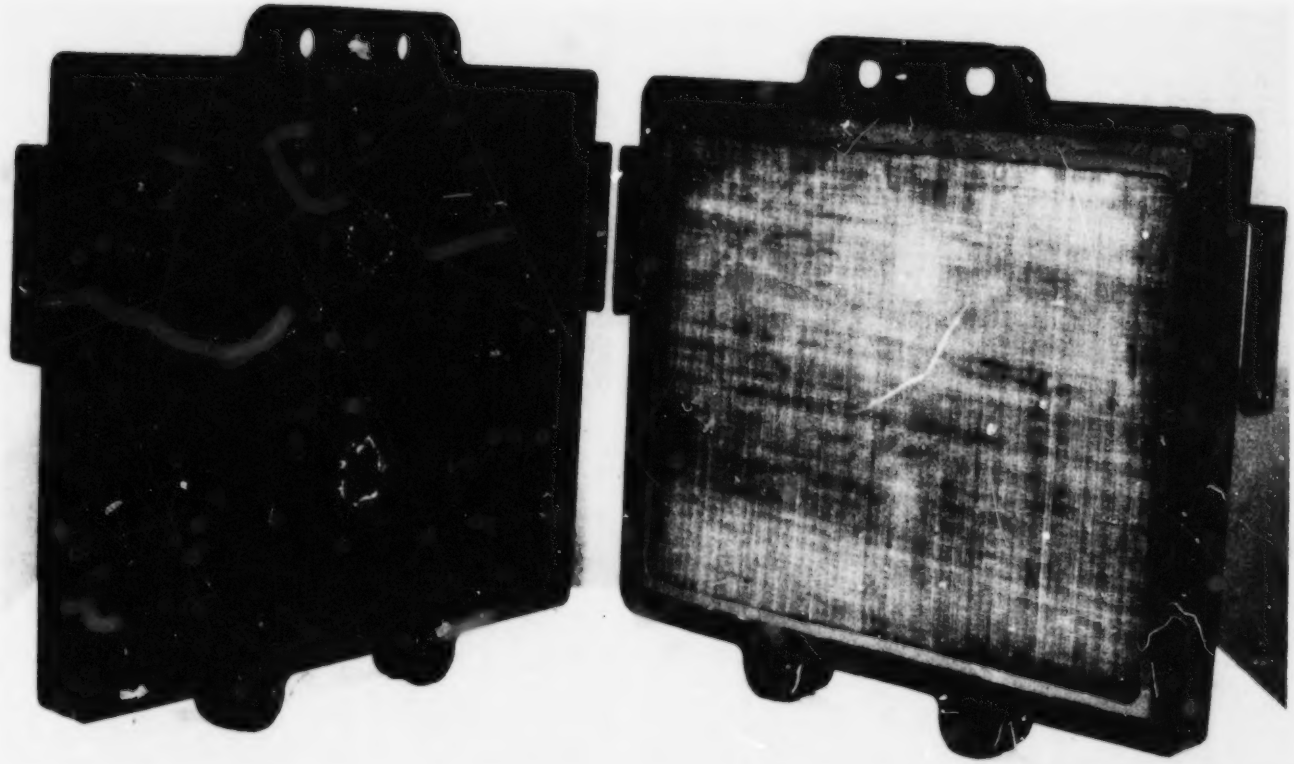

Figure 4. Basic Stack Components
Left: Cell Frame with anode attached
Right: Membrane package supported on cell frame

of the adjacent cell. A 3/8" wall in the center of the frame provides hydraulic isolation between cells. Electrical connection between the anode and the adjacent cathode is achieved by using special through-connectors which pass through two 1-3/4" diameter holes in the wall. These through-connectors carry about 265 amperes apiece while maintaining the hydraulic isolation between the compartments.

The compartments are fed from the 1" diameter manifolds at the bottom of the cell. The channel that leads from the manifolds at the compartment is drilled and tapped to receive a specially designed flow restrictor fabricated from Kel-F plastic (polytrifluorochloroethylene). The flow restrictors distribute the flow evenly to each compartment throughout the cell stack. The restrictor appears in Figure 3. The gases and electrolyte exiting from each compartment pass through four 1/2" diameter holes at the top of the compartment and into the product manifolds located at the top of the frame.

The anode is an expanded titanium screen coated with a special metal oxide coating. This is the so-called dimensionally stable anode or DSA. It rests in a recessed ledge in the face of the molded cell frame. The cathode is constructed from a sheet of expanded mild steel and is fitted in the other side of the cell frame in a similar manner.

The membrane package consists of an XR cation-transfer membrane laminated between 2 frames of 1/32" thick high temperature PVC, which have cutout portions corresponding to the active area of the cell and the manifold holes. A die-cut gasket of 1/16" ethylene propylene rubber is then bonded onto each side of the membrane frame to produce a combination membrane and gasket. The membrane package is fitted onto the face of the assembled cell block by slipping it over two 1/4" diameter nylon line-up pins that are fitted into holes drilled in the border of the cell frame. These line-up pins insure a proper alignment of all the components in the assembled stack.

The cell components are fitted into a skid mounted press similar to the type used for a plate-and-frame filter apparatus. The skid is shown in the process of construction in Figure 5. The hydraulic connections to the cell manifolds are made through the stationary end plate. Besides the cell the skid contains the pumps, filters, and product handling equipment required by the system. All feed piping is corrosion resistant PVC with no metallic components exposed to corrosion by the brine feed.

The cell effluent system, including the reactor, is mounted at the end of the skid directly adjacent to the fixed endplate. All of the components are constructed of either glass, PVC, or titanium. The lower portion of the chlorine seal leg is constructed of industrial glass piping to allow visual determination of the reactor operating pressure.

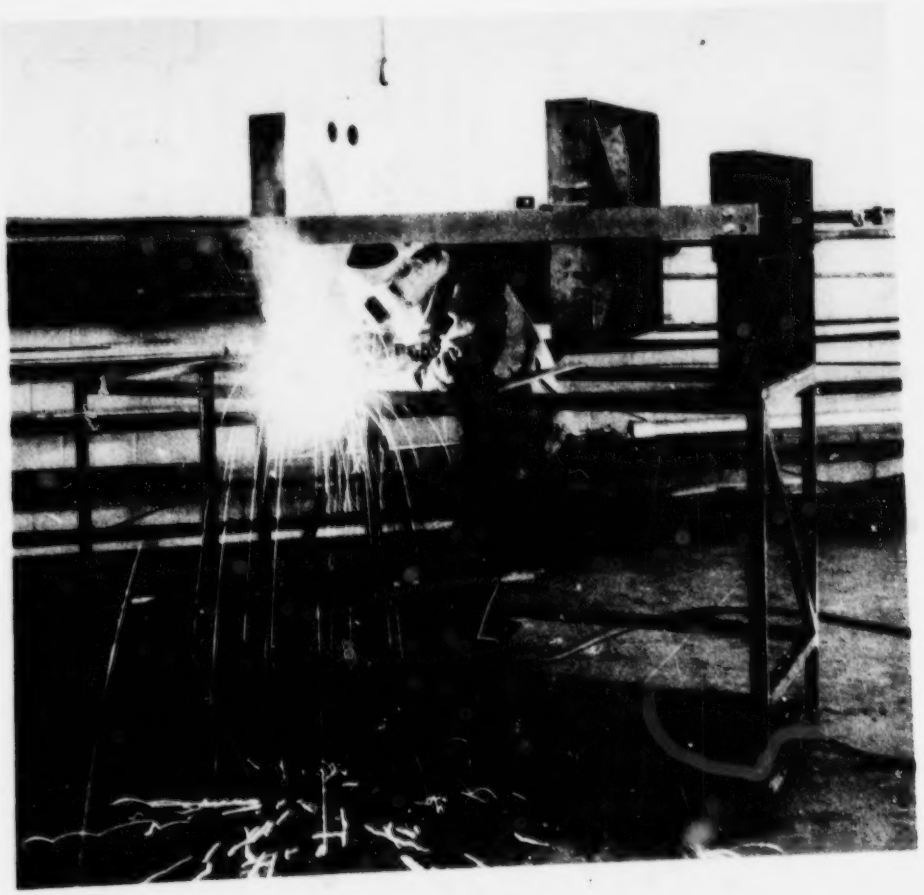

Figure 5. Cell Press and Skid in Process of Fabrication

Two Hastelloy level probes are also inserted in the seal leg to shut down the system if there should ever be a loss of liquid seal.

Figure 6 shows a detailed flow diagram of the final generator system. Saturated brine from the lixator is filtered and fed to the anolyte manifold of the cell stack by a positive displacement metering pump. The pressure of the feed stream is monitored to warn of a pump failure or clogged filter system.

The water feed to the cathode compartment is first reduced from standard city supply pressure to about 1 psi and then filtered and metered in a manner identical to that of the brine. Pressure sensors are also installed after the pumps to detect pump or filter malfunctions.

The mixture of chlorine and spent brine from the anolyte compartments of the cell system is fed to the chlorine seal leg assembly. The chlorine gas flows overhead to the reactor while the disengaged spent brine flows out of the seal leg by gravity.

The mixture of hydrogen and caustic from the cathode compartments is fed into the hydrogen disengager. The hydrogen gas is removed by means of a blower system which dilutes the hydrogen with air to well below its explosive limit and vents it to the atmosphere. The caustic solution is cooled in a shell-and-tube heat exchanger to about 30° C before it enters the reactor.

The reactor consists of a piece of 4" diameter PVC pipe approximately 40" in length. The caustic flows up from the bottom of the reactor and reacts with the chlorine also fed from the bottom. The resulting sodium hypochlorite solution overflows from the reactor outlet by gravity into an accumulation tank.

The chlorine gas is sparged into the reactor through a piece of 1" PVC pipe which projects into the solution from the top of the reactor. The pipe, drilled with a number of 1/32" sparge holes, has a 15 foot long, 1/4" diameter titanium cooling coil wrapped around it to absorb the heat of reaction. This reactor gives a reaction yield greater than 96%. For a short time during the startup of the unit there is insufficient caustic present to absorb all of the chlorine gas. To avoid undesirable operating conditions, the pH of the reactor effluent is monitored and additional caustic from an auxilliary supply is added whenever the pH drops below 8.0.

An electrical control panel provides for automatic start-up and shutdown of the hypochlorinator and has also provisions for emergency shutdown in case of equipment malfunction. In normal operation when there is a demand for hypochlorite, the control system sequentially turns on the blower system; turns on hydrogen detector, chlorine detector and pH control system; opens appropriate feed valves; starts pumping system;

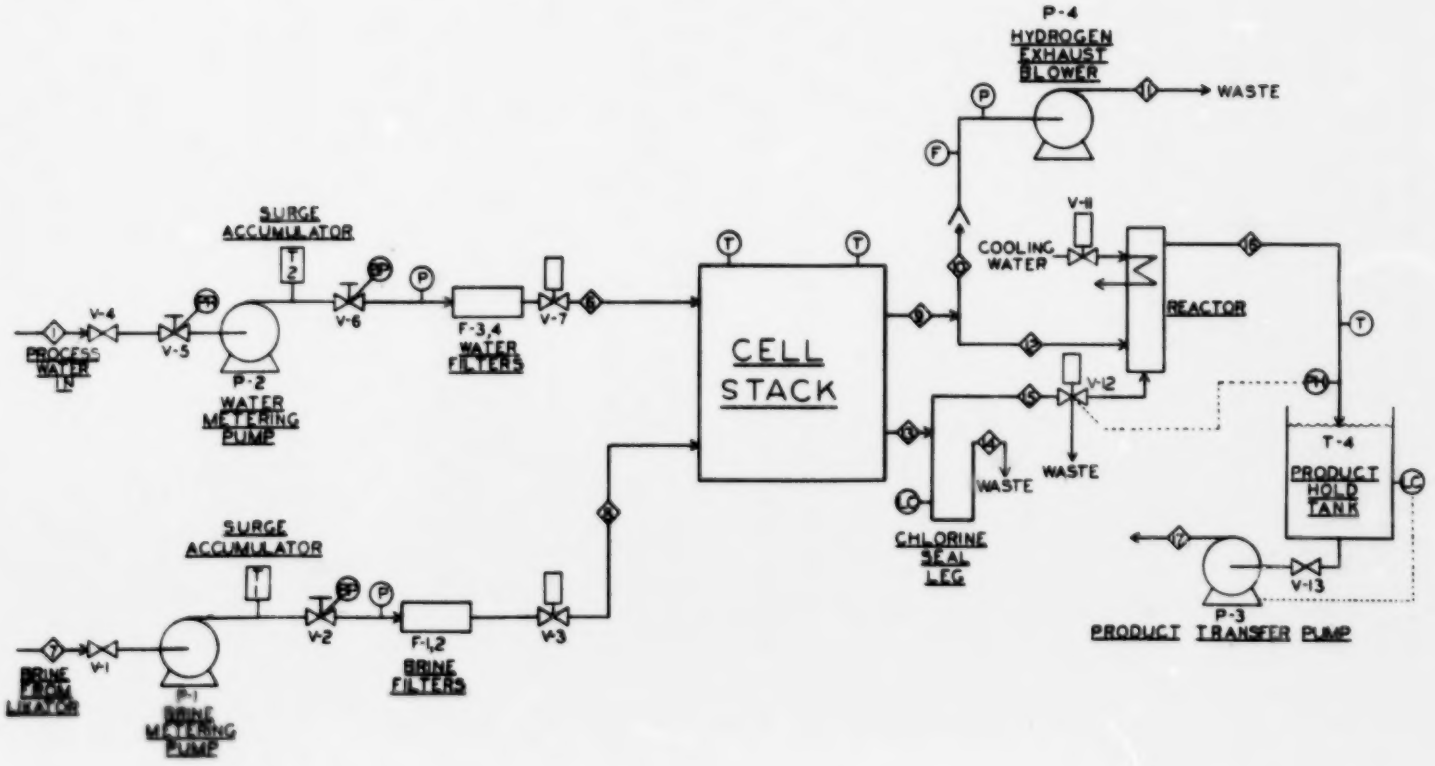

Figure 6. Detailed Flow Diagram

and turns on the rectifier. There is a time delay of 20 seconds before the safety interlocks are activated to allow the system to begin normal operation. After the system has operated for sufficient time to satisfy the hypochlorite demand, all of the equipment, except the hydrogen blower and the transfer pump is automatically shut down. The blower and transfer pump continue to operate for 10 minutes to insure that all of the hydrogen is vented and the hypochlorite has been forwarded to the storage tank.

The control panel also has interlocks to shut down the cell system if any of the following conditions occur:

- blower failure;
- high cell temperature;
- high reactor temperature;
- chlorine or hydrogen release;
- loss of seal in chlorine seal leg;
- high or low current limit;
- high pressure drop through filters;
- loss of pump pressure.

If any one of these conditions occurs, the system immediately shuts down and a malfunction light indicates the nature of the problem. An alarm horn is also activated to summon an operator. After the malfunction is corrected, the system can be restarted by means of a reset button.

The power supply was obtained from Enthone, Inc., Brooklyn, N.Y. The rectifier is of the saturable core type with a capacity of 1500 amps at 36 volts D.C. The rectifier has a stepless control over the range from 100 amps to 1500 amps and has safety features such as high and low current shutoffs and thermal overload protection.

Cell Operation

A number of operating conditions for the full scale cell were investigated to optimize temperature, efficiency, salt utilization, and voltage. The most favorable operating conditions are:

Cell Active Area	2.2 ft^2
Current	525 amps
Current Density	240 $amps/ft^2$
Cell Voltage	3.7-3.8 volts/cell

Cell Temperature	87 - 89° C
Brine Feed Rate	58 ml/min cell
Salt Utilization	81%
Water Feed Rate	110 ml/min cell
Caustic concentration	2.0 - 2.3 N
Hypochlorite Production Rate	135-140 ml/min cell
Overall Electrical Efficiency	77%

An overall mass balance for the operation of the hypochlorite generator is shown in Figure 7. This mass balance was derived from data taken during test runs of the full scale two cell stack. These data were then scaled up to represent the operation of the 12-cell module which is presently under construction. The data reflect operation at a current density of 240 ASF and a temperature of 86° C. The operating voltage of the cells under these conditions was 3.8 volts per cell.

Component Life

All of the critical components in the system have been tested in actual operation for over 3000 hours without any sign of deterioration or dunctional impairment.

Membrane - The XR membrane has been tested for more than 3000 hours at current densities between 200 and 400 ASF. In all of the tests that have been run on the present membrane there has been no membrane failure or any apparent attack on or deterioration of the material. Based on these tests it is felt that the membrane should last for at least two years in continuous service and probably considerably longer.

Electrodes - The DSA's have been run for the same period of time as the membranes. Only one anode failure was experienced during this program and that failure was attributable to obvious mistreatment during a test run. According to experience and based on data supplied by Electrode Corporation the anodes should have a minimum life of three years. After the end of this period the electrodes can be recoated.

Cell Frames - The cell frames are constructed from high temperature asbestos filled polypropylene. This material was tested extensively in both hot wet chlorine and caustic. It undergoes an initial surface attack which roughens and whitens the surface and results in a slight weight gain. No further attack is observed.

All of the auxiliary equipment in the system was chosen on the basis of maximum economical resistance to the operating conditions. In the test-

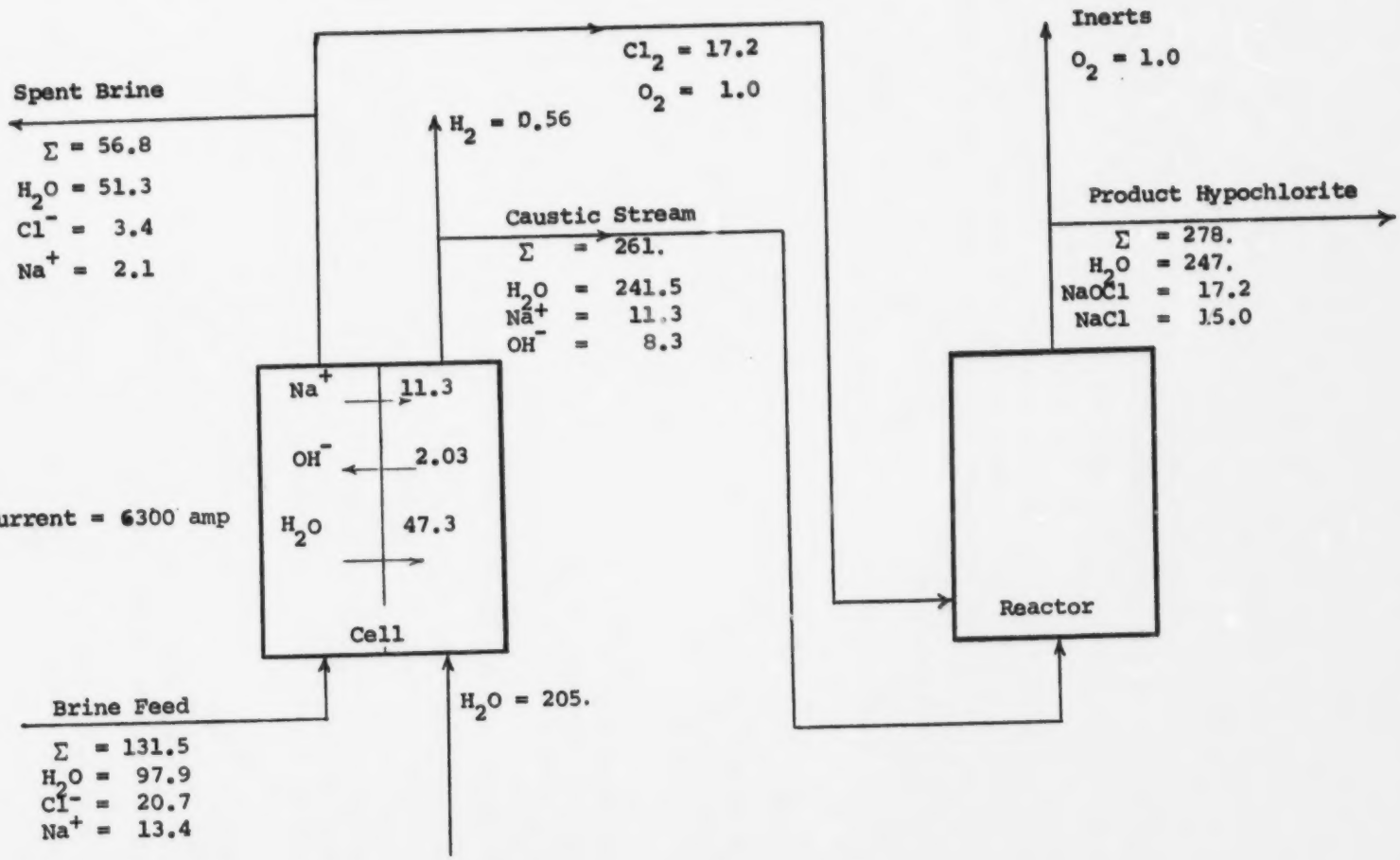

Figure 7. Mass Balance for Full Scale Hypochlorite Generator (based on data of 6.17.71). All flows in pounds per hour.

ing and evaluation period all of the components have performed satisfactorily.

System Economics

The overall economics are dependent on the size of the plant and the local costs of electrical power and salt. However two detailed cases will present an outline of the present economic picture. The first case is the actual installation of the twelve cell module at Somerville and the other will be a representative facility designed for continuous one ton per day production.

The field test unit was designed for installation in the Somerville Marginal Conduit Pretreatment Facility. This facility is being constructed to divert combined overflow, which was being dumped into the Mystic River basin, into the tidal portion of the river. All overflow is to be screened and disinfected with hypochlorite. The conduit will act as the detention chamber with a 9.5 minute contact time for the 5 year storm and progressively longer times for less severe loads.

The Somerville interception station has been designed on the basis of 240 hours per year or storm water overflow. The average flow of this overflow will be 90 MGD and the desired dosage level will be 4.3 ppm of sodium hypochlorite. The consumption of hypochlorite will be 32,200 pounds of chlorine equivalent.

A balance was made to determine the fraction of time the unit should operate. A high capacity unit, which runs a small fraction of the time would refill the storage tank rapidly but the capital cost would be high. A low capacity unit running almost constantly would decrease the unit cost but the refill rate might not be sufficient to handle two storms in close succession. A trade-off indicated a unit with a capacity of 15 lbs/hr would be near optimal. This unit would operate approximately 25% of the time.

Based on the volume and frequency of storms the generator system was designed for a capacity of 15 pounds of chlorine equivalent per hour. Since the yearly consumption is 32,200 pounds per year, the system will be running 2,400 hours per year or 27% of the time.

The yearly operating expenses of the hypochlorite generator at this installation are shown in Table 1.

Based on a yearly capacity of 32,200 pounds this results in an operating net of 9.1¢/lb of chlorine equivalent. At that location the quoted price for delivered hypochlorite is 15¢ per pound of chlorine equivalent.

Table 1

Yearly Operating Cost of the Hypochlorite Generator at Somerville,Mass.

Electricty			
	Demand Charge - 21 KW @ $20.6/KW		$1,298.00
	Usage Charge - 4,270 KWH/mo. @1.8¢/KW	863.00	
Salt	32.2 tons/yr @ $40/ton		$1,290.00
Water			13.50
	Process Water 50,000 gal/yr @ $0.15/gal	7.50	
	Cooling Water 40,000 gal/yr @ $0.15/gal	6.00	
Maintenance			325.00
	Replacement membranes	45.00	
	Replacement Anodes	30.00	
	Labor @ $5.50/hr	250.00	
	Total Operating and Maintenance Costs		$2,926.50

There are several factors in this application which make the production cost per unit of hypochlorite high at this location. Between the demand charge and the relatively low power usage in this application the cost per KWH is over 2.5¢. The salt used at the Somerville installation is a purified grade delivered in 100 pound bags. The cost per ton of salt is $40. Using a standard grade of bulk delivered salt the cost would drop below $20 per ton.

A more representative cost of operation of a generator installation is that estimated for a unit with a capacity of 1000 pounds per day operating 350 days per year. Economic assumptions in this estimate are: incremental power charge of 1.0¢ per KWH including demand charge, bulk delivery of salt at $15 per ton, negligible cost of process water (as indicated by the previous example), 175 hours of labor at a yearly cost of $1000, and amortization over 20 years at 5%.

The estimated costs under these assumptions are shown in Table 2. At an annual production rate of 3.5×10^5 pounds this results in an operating cost of 4.06¢ and a capital amortization cost of 1.37¢ per pound of available chlorine.

Capital costs will be higher with the electrochemical generator than with purchased hypochlorite. While capital costs can be estimated with

Table 2

Yearly Operating Costs of 1000 lb/day Hypochlorite Generator

Electrical Costs		$5900
Salt Cost		$5250
Maintenance		$3075
Membranes	1,245	
Anodes	830	
Labor	1,000	
Total Operating & Maintenance Costs		$14,225
Annual Amortization of Capital		$ 4,800

some accuracy, there is a wide divergence in methods of capital amortization. Estimated capital costs are shown in Figure 8.

It can be seen from the above illustrative cases that the hypochlorite generator is far more economical than delivered sodium hypochlorite and, in some cases, is almost competitive with liquid chlorine. Although the comparative costs vary depending on factors of size and location, the system offers significant economic advantages in a majority of cases.

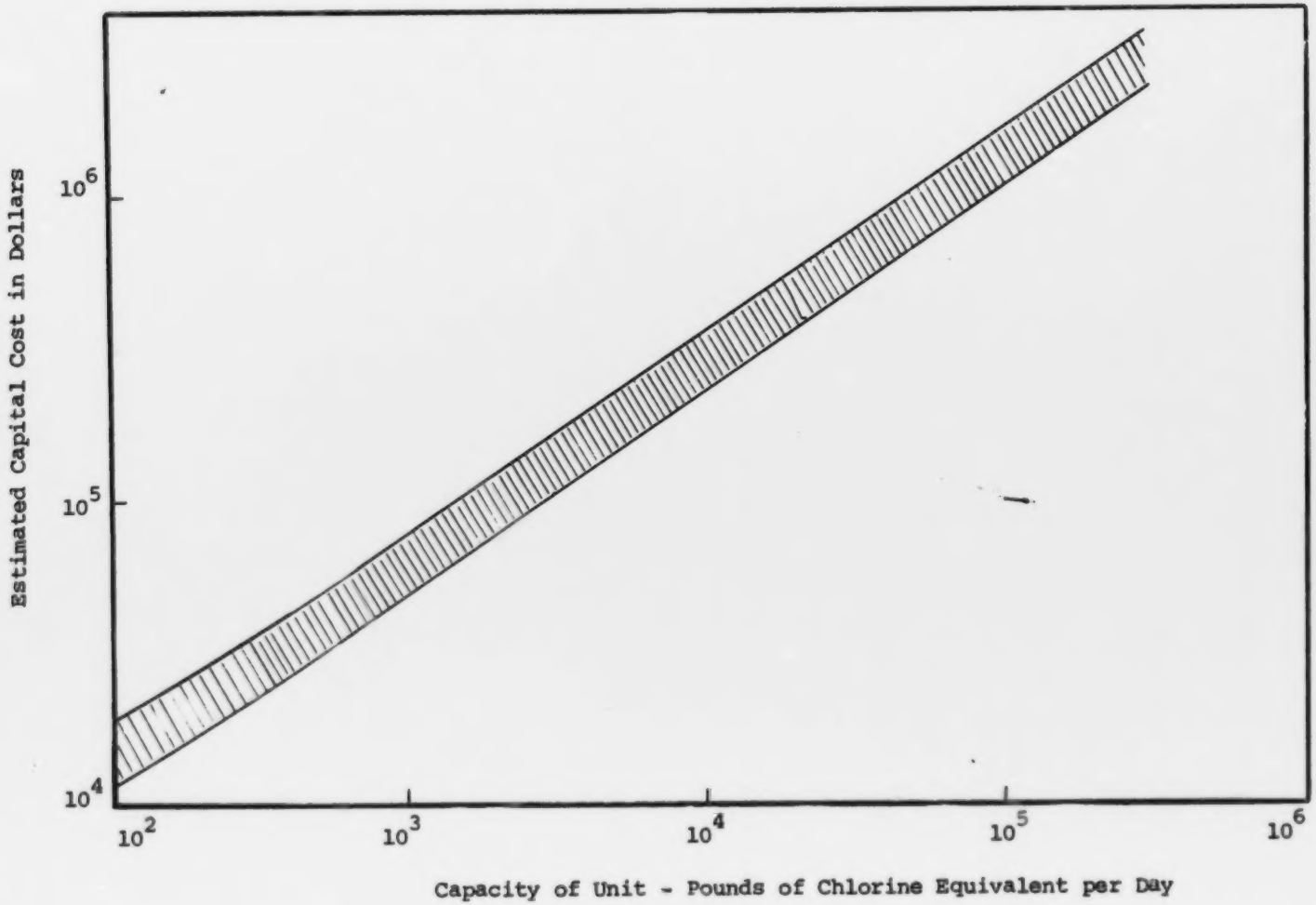

Figure 8. Estimated Capital Cost of Hypochlorite Generator

SECTION III

LABORATORY DEVELOPMENT

Throughout the development of the hypochlorite generator, three design criteria were considered to be of prime importance. These criteria were safety, economy, and simplicity of operation. These three principals were responsible for the path of development which the hypochlorite generator took in the transition from a 2 by 2 inch laboratory cell to the present system, which by modularization could be expanded to produce tons of chlorine equivalent per day.

Operational safety of the system was the most important consideration in the development of the hypochlorite generator. Any practical method, based on present technology, of producing sodium hypochlorite from sodium chloride results in the generation of chlorine gas, hydrogen gas and sodium hydroxide. Each of these products presents a potential hazard. To minimize these hazards the system was designed: , to contain a minimum inventory of hydrogen, chlorine or caustic; to minimize the possibility of contact between hydrogen and chlorine; to provide a safe means of disposal of the hydrogen gas; and to shut down automatically if any malfunction should occur.

The operating expense of the system depends primarily on the efficient use of two commodities, salt and electrical power. Real salt utilization is defined as the fraction of salt fed to the cell, or cell stack which is decomposed. Efficient use of salt requires that this be as high as possible. The efficient use of power requires a high current efficiency and a low cell voltage. Current efficiency as used here is the ratio of current theoretically required to that actually required per unit of product hypochlorite. The minimum values of current and voltage are 343 ampere hours per pound of chlorine and 2.15 volts per cell, the reversible cell potential. Any practical cell will operate above these values.

A factor which can affect the economics of the system is the cost of maintenance and replacement parts. If the system were to undergo replacement of electrodes or other components frequently, this would have an undesirable effect on the operating cost and possibly even decrease the overall capacity of the unit. It is then highly desirable to have long-life components, provided the lifetime is consonant with initial cost.

With regard to simplicity of operation, the hypochlorite generator diverges significantly from industrial practice. Most industrial caustic-chlorine cells require highly trained personnel as operators. Operation of these cells is based on delicate flow balances and close

monitoring of the systems operation. Since the hypochlorite generator is to be designed for unattended operation, it must be susceptible to automatic control including start-up and shut-down.

Electrochemical Cell

In a caustic chlorine cell, brine solution is fed into the anode compartment where chloride ion is discharged at the anode forming chlorine gas.

$$2\ Cl^- \rightarrow Cl_2 \uparrow + 2e^- \qquad (1)$$

At the cathode, water is electrolyzed producing hydrogen gas and hydroxyl ions.

$$2\ H_2O + 2e^- \rightarrow 2\ OH^- + H_2 \uparrow \qquad (2)$$

Current is carried through the electrolyte between the electrodes principally by sodium ion (Na^+). A separator is usually placed between the electrodes. The purpose of the separator is twofold. First, it provides a barrier that prevents the hydrogen and chlorine gases from coming into contact with each other. Second, it provides a hydraulic barrier to prevent hydroxyl ions from migrating into the cathode compartment.

A number of small scale cells were built and tested utilizing a variety of geometric configurations, electrode materials, and diaphragm materials. The small scale test apparatus is shown in Figure 9. A series of tests was run on each of these cells to determine current efficiency, operating voltage, and materials reliability.

The size of the experimental apparatus was chosen such that the production rate of chlorine would not be hazardous in the laboratory and yet the cell would be large enough to illustrate the effectiveness of materials and modes of construction, and performance would be representative of full scale operation.

The materials of construction for those parts other than electrodes in contact with chlorine gas or hypochlorite were Lucite or chlorinated polyvinyl chloride. The Lucite spacers allow visual inspection of the interior of the cell to determine ease of gas-electrolyte separation and electrolyte level. The experimental cell volume is 75 cm^3, and the active electrode area is 30 cm^2 for most tests.

The flow rates of water and brine to the cell were provided by positive displacement metering pump capable of $\pm$ 1% accuracy.

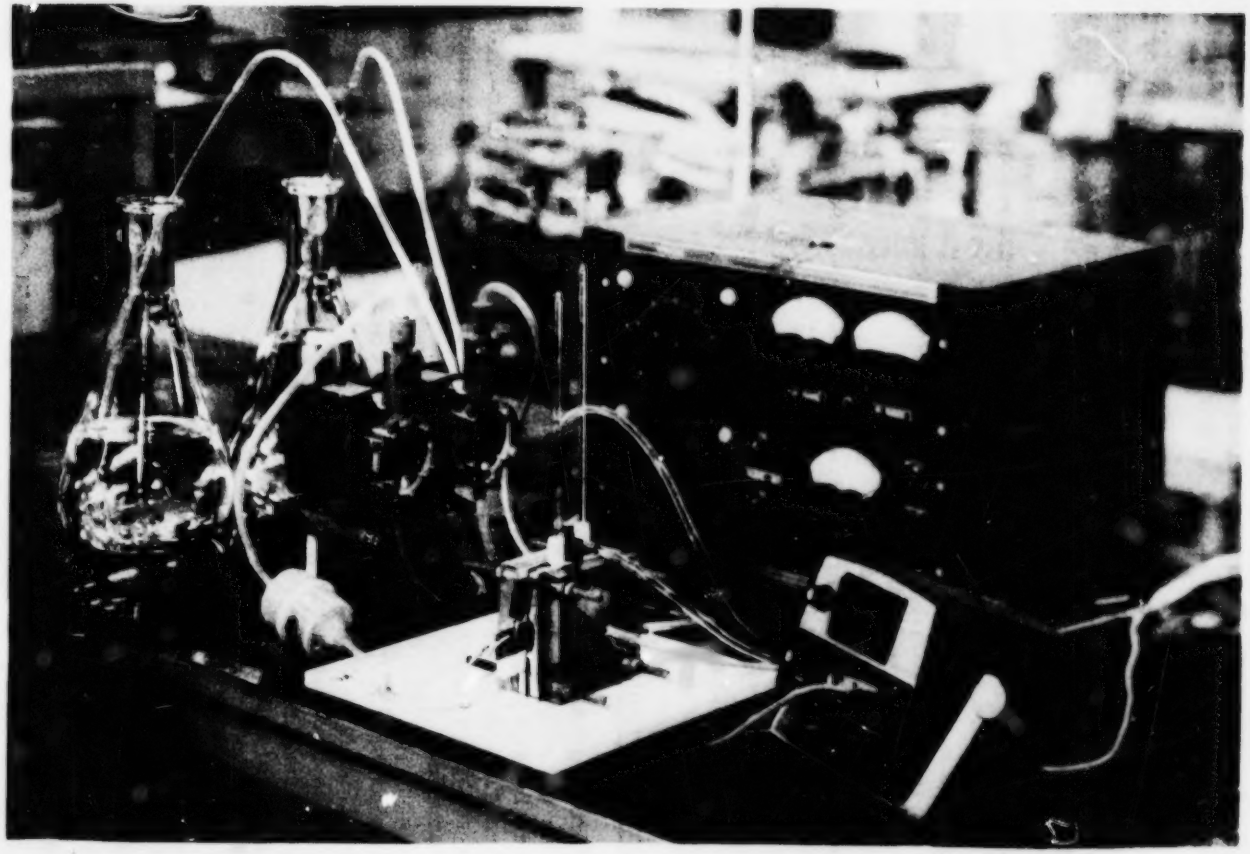

Figure 9. Small Scale Test Cell and Control Apparatus

In many single cell tests reference electrodes were introduced into the cells to allow separation of the voltage across the cell into anode and cathode potentials and resistive potential drop. Saturated calomel electrodes were used. These were connected ionically to the active electrode surfaces by Luggin capillaries. The various potentials in the cell were measured with a vacuum tube voltmeter.

Current efficiency was determined from the rate of production of free chlorine in the anode compartment expressed in gram equivalents per Faraday. The method of analysis of the anode compartment effluent is the Iodometric Method (1).

This experimental program showed that the most economical and practical design was a two compartment membrane cell with independent water feed to the cathode. The best anode was found to be the recently developed DSA (dimensionally stable anode) and the most acceptable cathode was found to be mild steel.

Based on the very favorable results from the small scale cell testing, work was begun on developing and testing a full scale model. This was followed by testing of a two-cell stack and finally the 12 cell module was constructed. Experimental work on each phase of this development is described in subsections below.

Cell Configuration

The internal geometry of the electrochemical cell is a compromise between the conflicting requirements that the resistance of the electrolyte path be low and that hydroxyl ion (OH^-) generated at the cathode not migrate to the anode. In a high current density caustic-chlorine cell, a separator prevents bulk mixing of the solutions surrounding the two electrodes.

Migration of hydroxyl ion into the anode compartment can reduce the current efficiency of the cell in several ways. The pH of the anolyte usually runs between 3 and 4. Significant migration of OH^- into the anode compartment causes this to increase and increases the occurrence of oxygen evolution at the anode.

$$H_2O \rightarrow 1/2\ O_2 \uparrow + 2H^+ + 2e^- \qquad (3)$$

Increased pH also increases the amount of hypochlorite in the anolyte by affecting the equilibrium:

$$Cl_2(aq) + H_2O \rightleftarrows HOCl + Cl^- + H^+ \qquad (4)$$

which increases the probability of chlorate formation:

$$3HOCl \rightarrow ClO_3^- + 2Cl^- + 3H^+ \qquad (5)$$

The products O_2 and ClO_3^- are essentially useless for disinfection. The electrochemistry of chlorate formation is discussed in detail in References (2) and (3).

Basically, three cell configurations were studied, the diaphragm cell, the membrane cell and the three compartment cell containing both membrane and diaphragm.

Use of an open cell without diaphragm was briefly considered. However current efficiencies observed ranged from 25% to a high of 55%. High velocity operation which was not tested, would increase the efficiency, but it would not be possible to produce hypochlorite of sufficient concentration for practical storage.

Diaphragm Cell

The distinctive feature of a diaphragm cell is a porous diaphragm, usually asbestos, which separates the anode and cathode compartments. This is shown in Figure 10. Brine is fed into the anode compartment and flows through the diaphragm into the cathode compartment. The hydraulic flow through the diaphragm is set at a rate that prevents the hydroxyl ions from migrating into the anode compartment. Current efficiencies around 90% can usually be obtained.

The diaphragm cell does however have an important disadvantage. Since chlorine and caustic are both extremely corrosive materials only a few diaphragm materials will survive in the cell environment. Traditionally asbestos has been used but it lacks mechanical strength. Other materials which exhibit high corrosion resistance, i.e., Teflon, if fabricated into a diaphragm, usually exhibit high electrical resistance which is undesirable.

Another drawback of diaphragm cells is the necessity for close hydraulic control. There are two flows out of the anolyte compartment, chlorine gas product and anolyte liquid flowing through the diaphragm. To prevent chlorine gas flow across the diaphragm and to avoid flow of anolyte liquid out with the chlorine gas, a hydraulic balance must be maintained at all times. Since the pressure drop across the diaphragm increases with time, skilled operators are needed to monitor and adjust the typical caustic-chlorine cell.

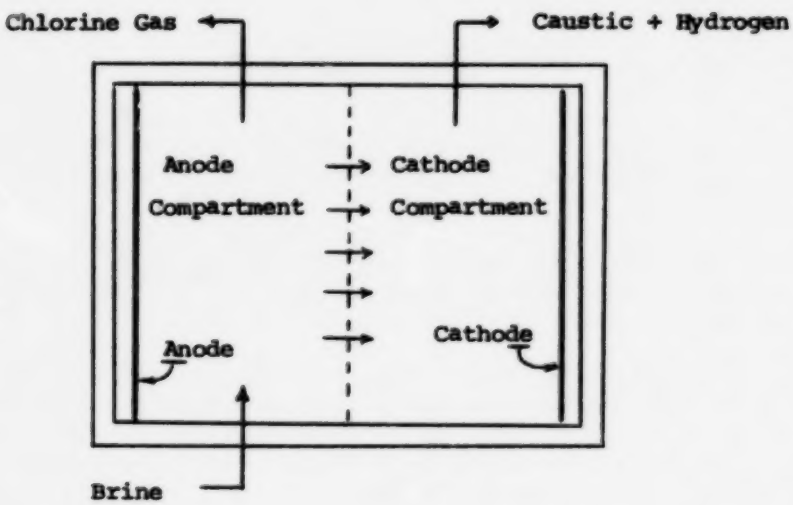

Figure 10. Diaphragm Cell with Sheet Electrode

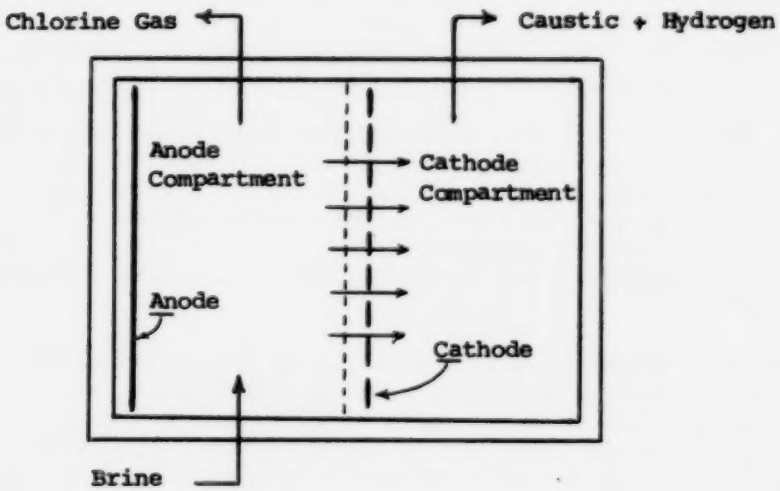

Figure 11. Diaphragm Cell with Expanded Cathode

Probably the most critical component in a diaphragm cell is the diaphragm itself. The diaphragm must be chemically inert, have uniform pore size, prevent the caustic generated at the cathode from migrating into the anode compartment, and have low electrical resistance. For many years the caustic-chlorine industry has used slurry-deposited asbestos diaphragms against a porous steel cathode. Because of the requirement of minimum cell maintenance, the slurry deposited diaphragm, which requires skilled manpower at the installation is undesirable. Consequently, considerable effort was expended in the search for a suitable throw-away diaphragm which could be easily replaced.

A program was undertaken to evaluate the ability of various diaphragm materials to keep hydroxyl ions away from the anode and their short-term resistance to degradation. The chlorine current efficiency of a cell is directly proportioned to ability of the diaphragm to act as a hydroxyl barrier. The current densities studied in these tests ranged from 100 to 500 ASF which covers the probable range of interest. The diaphragm materials under consideration were porous polyethylene (Porex Corp.), porous Teflon (Chemplast), woven Teflon (Stern & Stern, Inc.), fuel cell and electrolytic grades of asbestos (Johns-Manville Corp.), polypropylene battery separators (National Lead Corp.) and polypropylene matte (Pellon Corp.).

These diaphragms were tested in cells like those shown in Figure 10 with sheet electrodes placed 2.5 cm apart. The brine feed rate in these tests corresponded to 50% nominal salt utilization. The anolyte was maintained at a slight hydraulic head, 1 to 2 feet of water, above the catholyte. The hydraulic head required to maintain proper flow through the diaphragm depended on the porosity of the diaphragm.

The various diaphragm materials studied were supported with polypropylene cloth on the catholyte side of the diaphragm and glass cloth on the anolyte side. Only those diaphragm materials having considerable strength were used without support. Table 4 presents the experimental data obtained from a number of porous diaphragm materials. Figure 12 shows the internal voltage drop for various diaphragm materials over the current density range 200 to 500 ASF. A minimum voltage curve is included as a reference in this figure. The minimum voltage is that which would exist across the electrode gap with concentrated brine at the operating temperature and current density without any diaphragm. The fuel cell grade asbestos contributes almost nothing to the overall internal resistance. The desirable properties of this material were confirmed in a variety of subsequent tests.

Electrochemical performance of this type of cell is characterized by the relationship between cell voltage and current density and by the relationship between current efficiency and salt utilization. The effect of current density on salt utilization is small. These relationships are shown in Figures 13 and 14.

Table 3

Evaluation of Diaphragm Materials

Diaphragm Material	Current Density ASF	Total Cell Voltage, volts	Resistive Voltage Drop volts	Current Efficiency (%)	Cell Temp. °C
Teflon Cloth	100	5.0	-	55.5	25
" "	150	-	-	59.	40
" "	200	5.4	-	56.	35
" "	350	7.6	-	52.1	30
" "	400	7.2	-	46.4	48
Porous Teflon (Zitex E-1002)	200	5.2	1.75	25.7	36
" "	300	5.9	2.28	66.7	42
" "	400	6.5	2.80	66.7	52
Porous PVC (Yuasa 0202G)	200	4.6	1.4	64.2	73
" " "	200	4.8	1.35	73.7	50
" " "	300	6.0	2.4	17.5	56
Porous PVC (Yuasa 620G)	200	5.3	1.7	47.7	40
" " "	200	5.1	1.25	51.6	38
" " "	200	5.1	1.65	76.4	38
" " "	300	5.7	2.1	36.0	50
Polypropylene Battery Separator (Polysep 40)	300	5.9	2.65	26.1	49
Electrolytic Asbestos 0.006"	200	5.3	1.5	84.3	39
" " "	300	6.2	2.05	74.9	43
" " "	400	-	-	71.5	51
Electrolytic Asbestos 0.010"	200	5.1	1.55	70.8	42
" " "	200	5.7	1.85	80.9	35
" " "	300	6.7	2.55	77.7	45
" " "	400	7.2	2.65	84.2	53
" " "	500	8.0	3.6	75.8	62
Electrolytic Asbestos 0.018"	200	4.35	-	59.0	59
" " "	200	-	-	52.5	60
" " "	200	-	-	91.	60
" " "	300	4.85	-	52.3	59
" " "	300	-	-	76.5	53
" " "	300	-	-	67.5	53
" " "	300	4.3	-	57.5	60
" " "	300	4.3	-	73.0	60
" " "	400	5.9	-	45.1	59
" " "	400	6.9	-	66.0	60
Electrolytic Asbestos 0.023"	200	5.1	1.6	85.3	43
" " "	300	6.0	2.65	82.2	40
" " "	400	6.9	3.65	77.5	55
" " "	500	7.7	4.35	74.4	63

Table 3 (Continued)

Evaluation of Diaphragm Materials

Diaphragm Material	Current Density ASF	Total Cell Voltage, volts	Resistive Voltage Drop volts	Current Efficiency (%)	Cell Temp. °C
Fuel Cell Asbestos 0.010"	100	4.8	-	86.	40
" " " "	200	5.9	-	89.5	55
" " " "	200	4.8	-	70.5	51
" " " "	200	4.8	-	86.5	51
" " " "	200	4.9	1.6	87.4	48
" " " "	200	5.8	1.37	87.2	40
" " " "	200	4.8	1.5	93.9	44
" " " "	300	5.55	-	85.7	53
" " " "	300	5.7	2.3	92.5	50
" " " "	300	6.2	1.9	78.5	46
" " " "	300	5.8	2.35	90.4	45
" " " "	400	6.1	-	83.0	56
" " " "	400	6.6	2.5	92.3	48
" " " "	400	7.1	2.25	63.9	56
" " " "	400	6.2	2.6	95.5	51
" " " "	500	6.8	-	87.6	60
" " " "	500	7.0	2.95	91.7	55

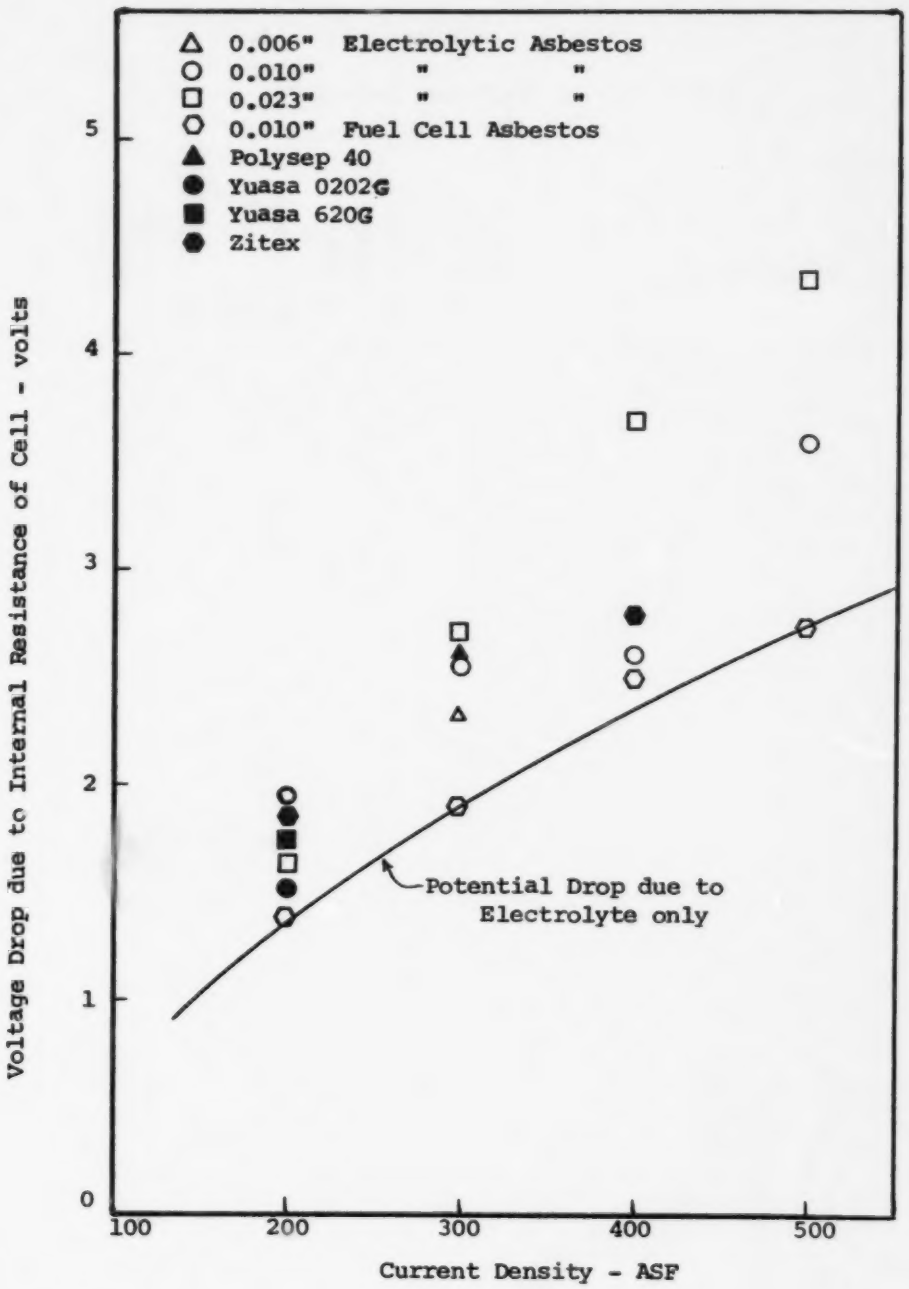

Figure 12. Effect of Diaphragm Material on Internal Cell Resistance

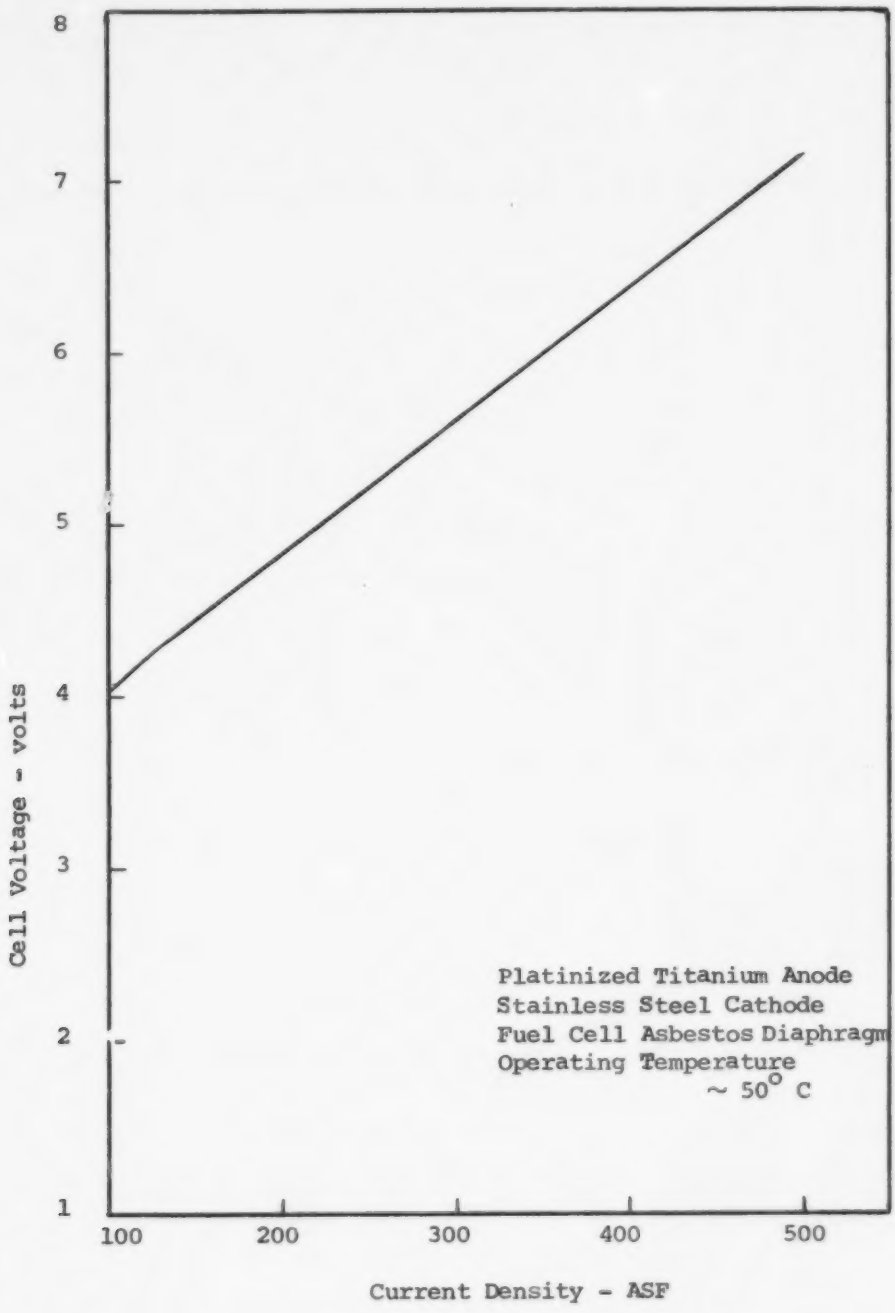

Figure 13. Typical Voltage-Current Curve for Sheet Electrode Diaphragm Cells

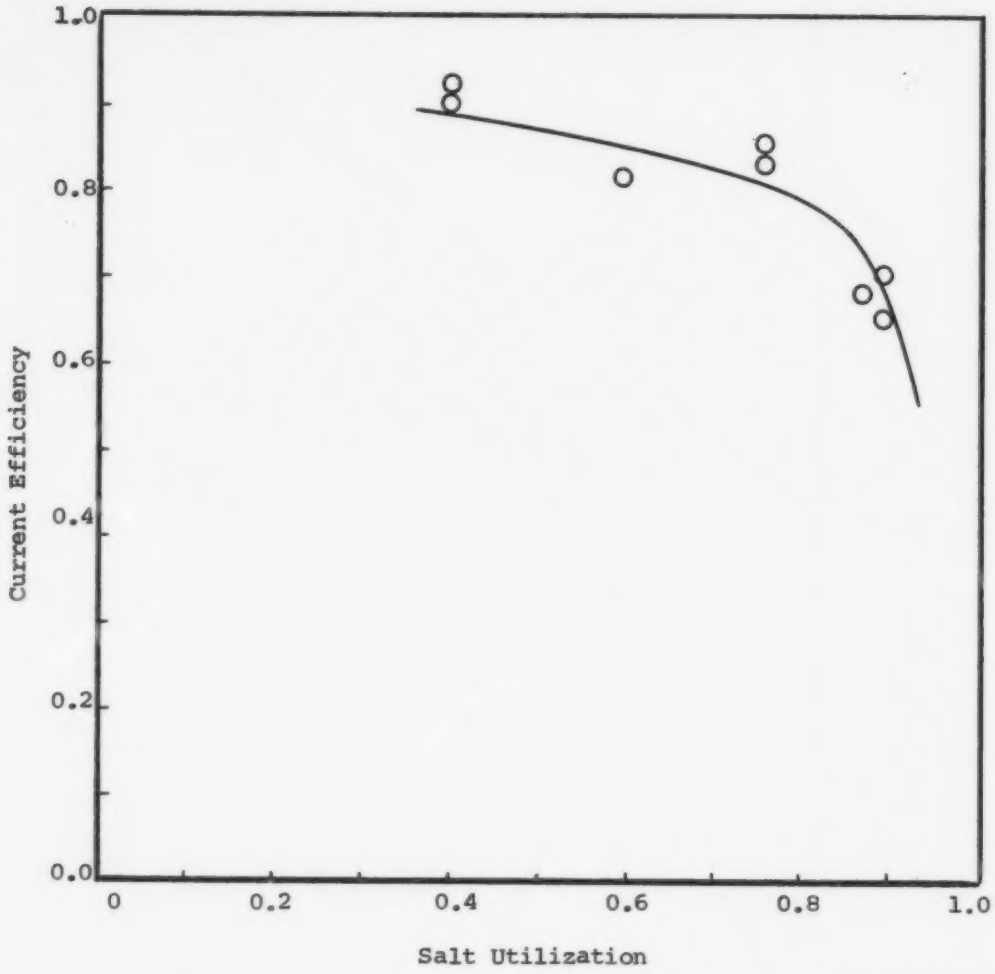

Figure 14. Effect of Salt Utilization on Current Efficiency for Sheet Electrode Diaphragm Cell

In the region of interest the relationship between cell voltage in volts, V, and current density in ASF, i, is linear and can be closely represented by:

$$V = 3.30 + 0.0077i \qquad (6)$$

Experimentally it is much more convenient to use nominal salt utilization than real salt utilization. Nominal salt utilization is defined as the fraction of salt fed to the cell which would be decomposed if the current efficiency were 100%. It is then equal to real salt utilization divided by current efficiency. "Salt utilization" without qualification refers to nominal salt utilization in this report.

Expressing current efficiency, η, and nominal salt utilization, f, fractionally, the data in Figure 14 can be expressed by:

$$\eta = 1.01 + 0.33 \log (1-f) \qquad (7)$$

These expressions are necessary for the computer optimization discussed in Section IV.

Diaphragm Cell with Expanded Cathode

Use of an expanded cathode is a refinement of the sheet electrode cell construction. This is shown in Figure 11, page 28. The drawing is placed next to that of the sheet electrode cell to facilitate comparison. This configuration allows the cathode to be placed next to the diaphragm which reduces the inter-electrode spacing and the internal resistance of the cell.

To permit leak-tight assembly in the cell, an ethylene-propylene rubber gasket was formed around the expanded nickel cathode.

The current efficiencies with this cell configuration were generally lower than the 85 to 90% observed with the sheet electrode (at 200 ASF with a fuel cell asbestos diaphragm). A high concentration of hydroxyl ion exists at the cathode surface. If the diaphragm sees this concentration, the current efficiency may be lowered. Several techniques were used to provide a slight separation between cathode and diaphragm in order to aid transport of hydroxyl ion away from the diaphragm. Results of these tests are given in Table 4. In all tests the cell voltage is lower than that of the sheet electrode cell.

The best current efficiency obtained was 85% using a polypropylene screen spacer between the diaphragm and the cathode. The polypropylene screen is constructed with vertical ribs 0.025 inches thick and with

0.25 inch spacing between ribs; the horizontal crosslinks are 0.008 inches in diameter. In addition to the spacer, a row of 1/8 inch holes was punched along the top and the bottom of the cathode to aid the circulation of electrolyte through the space between the cathode and diaphragm.

Table 4

Effect of Separation on Expanded Cathode Cell

Type of Separation between cathode and diaphragm	Current Density ASI	Cell Voltage volts	Operating Temperature °C	Current Efficiency %
No separation	200	3.7	55	35
No separation	200	4.2	65	76
0.020" separation	200	4.2	-	76
0.025" Saran Screen	200	4.65	63	53
0.025" polypropylene screen	200	3.60	-	85

It was felt that the relatively small mesh of the expanded cathode (Exmet #5/0-1/32" holes) might have caused low current efficiencies. An expanded cathode having somewhat large holes (Exmet #3/0-1/16" holes) was tested. The larger holes were expected to permit greater circulation of electrolyte around the cathode and reduce the hydroxyl ion concentration near the diaphragm. Current efficiencies with the larger mesh ranged from 81 to 92%.

In this configuration, when the cell was not being operated, the nickel cathode suffered severe attack. This attack was more pronounced with the expanded cathode than with the sheet cathode, presumably because of the great number of surface irregularities. Without an applied potential, the cell becomes a galvanic cell with the nickel becoming the anode. Salt deposits on the cathode were found to contain large amounts of nickel by emission spectrum analysis. If this sort of cell were to be used, it might be necessary to drain the cells, or maintain a potential between the electrodes when not in use.

The relationship between salt cut and current efficiency was determined using the best expanded cathode and diaphragm configuration. This curve is shown in Figure 15. The relationship between salt utilization, f, and current efficiency, η , is reasonably expressed by:

$$\eta = 1.10 + 0.805 \log (1-f) \qquad (8)$$

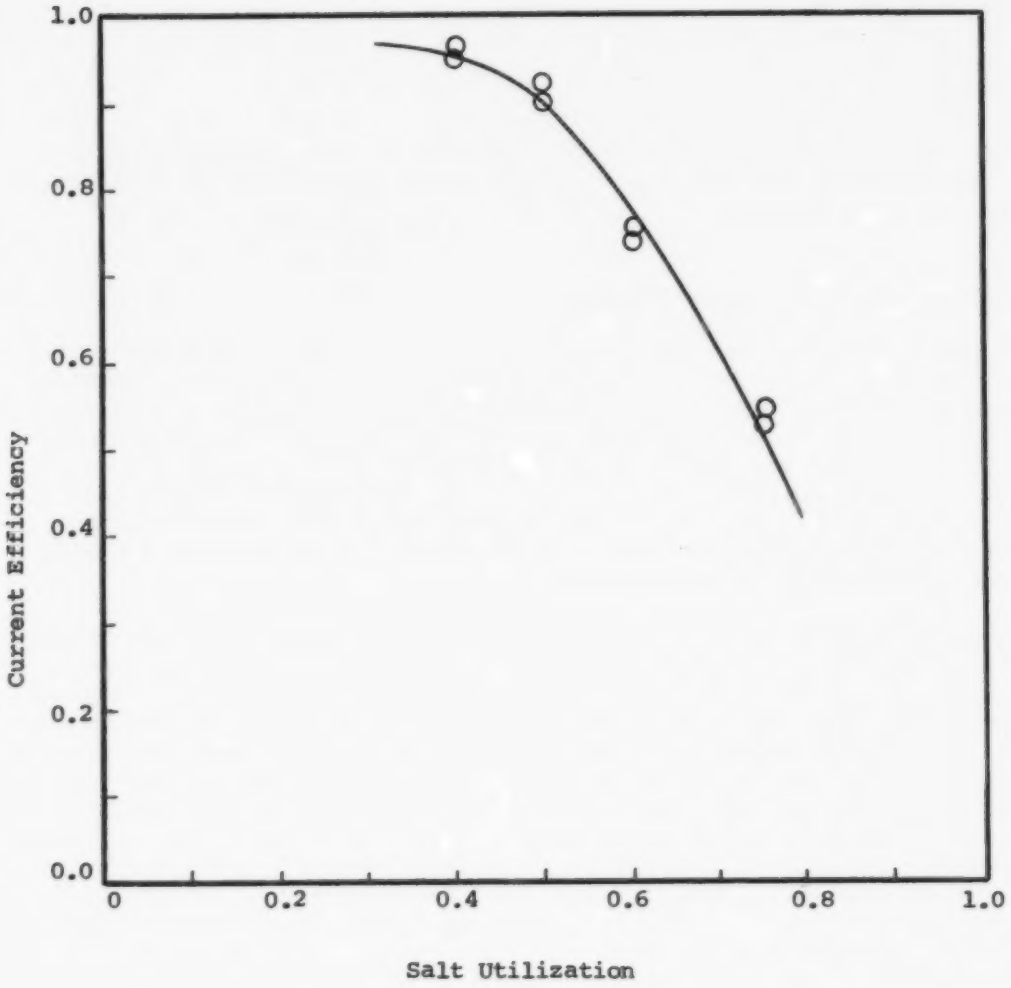

Figure 15. Effect of Salt Utilization on Current Efficiency for Expanded Cathode Diaphragm Cell

The current efficiency at high salt cuts using the expanded cathode is slightly higher at modest salt utilization and much lower at high salt utilization than with the plate cathode.

The relationship between voltage, V, and current density, i, can be approximated by:

$$V = 3.3 + 0.0036i \qquad (9)$$

The computer optimization indicated that this cell would operate at higher current densities but at higher total costs than the cell with two plate electrodes.

Difficulties with Diaphragm Package

To permit simple field replacement of the diaphragm, it was considered desirable to have a gasket diaphragm package. A frame of ethylene-propylene rubber (EPR) was compression molded around a fuel cell asbestos sheet. However, during a life test, it was noticed that carbonaceous deposits tended to collect on the diaphragm. The most likely source of this material was from the EPR portion of the composite diaphragm. The EPR rubber showed definite signs of chemical attack. Apparently the carbon filler in the EPR was being released into the anolyte and was being filtered on to the diaphragm.

Several possible solutions to the problem were tested. The EPR rubber was coated with a 3% solution of vinyl chloride-acrylonitrile copolymer (dynel) in acetone. This coating appeared effective for only two days operation. Two other procedures were more successful. The EPR rubber portions of the composite diaphragm were replaced entirely with acrylic polymer. In a similar procedure acrylic polymer was substituted for EPR only where wet chlorine would be likely to contact the gasket thereby retaining the resilient qualities of EPR necessary for effective sealing. Fabricating satisfactory diaphragm packages using acrylic resin was impeded by bubble formation in the plastic. This resulted from the presence of a volatile component in the acrylic molding resin. Bubble formation was virtually eliminated by reducing the molding temperature below that suggested by the manufacturer.

These diaphragms failed after approximately 200 hours of life testing. The mode of failure, however, was due to lack of wet strength on the part of the asbestos rather than to failure of the acrylic gasket.

The most serious problem was the rather unpredictable variation of wet strength from sample to sample. Early in the program a piece of fuel cell grade asbestos had a life in excess of 1200 hours. Later testing of the same type of diaphragm resulted in a significantly shorter life.

The supplier, Johns-Manville Co., indicated that the samples were the same type and quality during the test period. The mode of failure of the diaphragm was sagging of the asbestos which left holes in the diaphragm.

Before computer optimization was applied to the system, the hypochlorite generator was expected to operate only 200 to 450 hours/year. With annual replacement of the diaphragm on a routine basis, 1200 hours would be a satisfactory diaphragm life but 200 hours would be insufficient. The computer study indicated that production of hypochlorite solution at lower rates would be cheaper overall. This lower rate of production would require that the cells be running from 1000 to 4000 hours/year. Under these conditions a much longer diaphragm life, in fact longer than the best life observed,is required.

Several attempts were made to create a composite sandwich diaphragm in which an integrally bonded Teflon cloth would support the asbestos paper to overcome its lack of wet strength. Several problems were experienced in making these composite diaphragms. One problem was excessive flashing of rubber into the diaphragm portion of the composite. This ruined the porosity of the resulting diaphragm. Flashing was overcome by carefully measuring the amount of uncured rubber in the center of the mold. Movement of the Teflon cloth was overcome by cutting the Teflon cloth larger than the outside dimensions of the mold and maintaining tension on the cloth during molding. After the molding operation was completed, the excess Teflon cloth was trimmed away. An intermittent problem was the apprearance of pressed wrinkles in the asbestos cloth which resulted in holes in the resulting diaphragm.

Another approach to the asbestos support problem was to sew the Teflon cloth and diaphragm together with Teflon thread in a criss-cross fashion to create a quilted sandwich of Teflon cloth and asbestos. This failed because of the holes which the needle left in the asbestos sheet.

During the time when the diaphragm cell was under active consideration, no totally satisfactory diaphragm was developed. The necessity of this development was obviated when the benefits of the membrane cell, described below, were discovered.

Membrane Cell

In a membrane cell, Figure 16, the anode and cathode compartments are separated by a cation exchange membrane. This membrane must have good chemical resistance since it is exposed to caustic on one side and freshly generated chlorine on the other side. There is no direct hydraulic flow from the anode to the cathode compartment. The only water that crosses the membrane is endosmotic water which is associated with the ions being transferred. The anolyte liquor and the chlorine

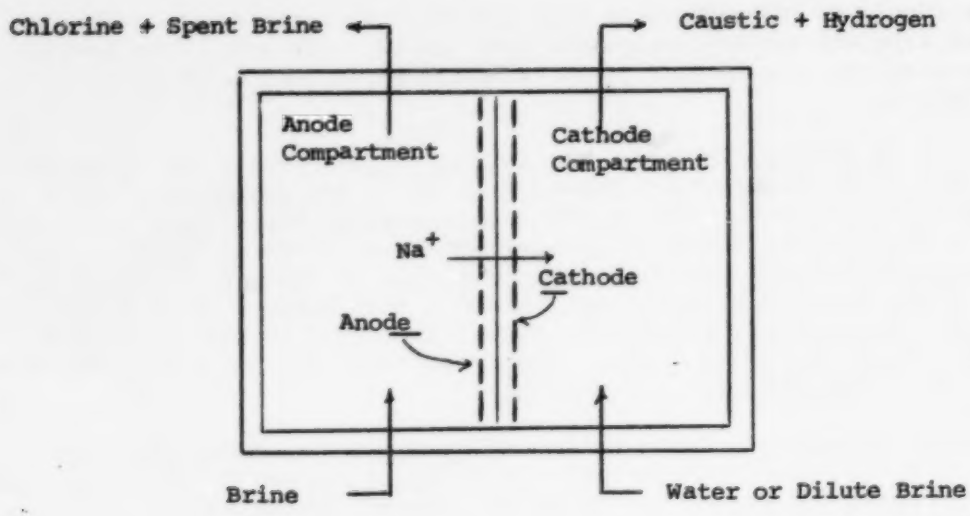

Figure 16. Membrane Cell with Expanded Electrodes

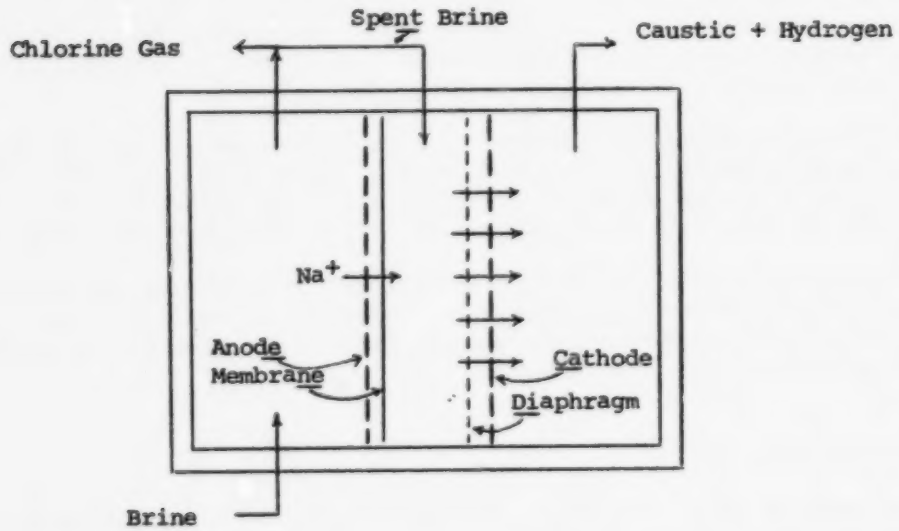

Figure 17. Three Compartment Cell

exit from a common port and are sent to a gas-liquid separator where the product chlorine gas is separated from the depleted brine. Since there is no delicate pressure differential to be maintained, this cell does not have the hydraulic flow and control problems associated with a diaphragm cell.

A cathode feed stream is needed to sweep out the sodium hydroxide that is produced. This stream can consist of either fresh water or the disengaged anolyte solution. In the experiments performed with membrane cells, feed rates to the cathode compartment were used which resulted in formation of caustic solution between 0.5 and 4.5 N in the cathode compartment.

The major difficulty with a membrane cell is that fact that state-of-art membranes allow more back-migration of hydroxyl ions into the anode compartment than a good diaphragm, with a corresponding reduction of current efficiency. With the membrane cells used in this study, the optimum concentration of caustic in the cathode compartment has been about 10%, or slightly over 2N, and the resulting current efficiency, based on gaseous chlorine, was approximately 65% to 75%. The reason that "gaseous" is emphasized is that in a cation membrane cell a large fraction of the OH^- that migrates across the membrane reacts with the chlorine product, producing hypochlorite. The hypochlorite ion is reported as "Free Chlorine" in standard tests but it does not necessarily appear in the product hypochlorite. Thus when the total anode product (liquid and gas) is analyzed, the indicated current efficiency is higher than when the gaseous product alone is measured. The conclusion that may be drawn from these results is that although the membrane cell overcomes the primary disadvantages inherent in diaphragm cells, these advantages are obtained at the expense of current efficiency. Two modes of operation were investigated:

- Mode I - spent anolyte fed to the cathode compartment
- Mode II - water or dilute brine fed to the cathode compartment

In mode I saturated brine is metered to the anode compartment and the exiting stream is separated into liquid and gas phases. The liquid phase, which is depleted brine, is fed by gravity to the cathode compartment. This system has the advantage of being simple since it requires only one feed pump and does not require flow balancing. There are the disadvantages that caustic concentration cannot be varied independently of salt utilization and that the salt that is not decomposed in the anode compartment cannot be recovered.

A full series of tests on the small scale membrane cells operating in mode I was made. The various relationships that were found in this series of tests are outlined below.

In this mode of operation the normality of the caustic produced is strictly a function of the caustic current efficiency and the salt utilization. The experimental relationship between caustic normality, c, and salt utilization, f, is shown in Figure 18. The caustic normality is almost zero at zero salt utilization and increases linearly to approximately 4.0 at 100% salt utilization. This can be expressed as:

$$c = 0.0697 + 4.20\ f \qquad (10)$$

Product hypochlorite concentration is consequently also a unique function of salt utilization.

Figure 19 shows the relationship between current efficiency and salt utilization. The current efficiency decreases with increasing salt utilization from a high of about 85% current efficiency at very low utilization to a low of less than 65% at high utilization. Expressing current efficiency as η , the data closely correlate to:

$$\eta = 0.879 - 0.241\ f \qquad (11)$$

The two dependent variables, caustic normality and current efficiency, are then related by:

$$\eta = 0.883 - 0.0574\ c \qquad (12)$$

In mode II water or dilute brine is fed to the cathode compartment of the two compartment membrane cell. In this type of cell, current efficiency improves as the sodium hydroxide concentration in the cathode compartment is lowered. Current efficiency also improves somewhat with increasing chloride concentration in the catholyte. By maintaining a separately metered feed to the cathode compartment, the current efficiency can be controlled independently of the salt utilization. Another advantage of this method is that the depleted brine can be recirculated to the lixator for resaturation. Using this flow scheme it is possible to obtain 100% salt utilization. Although this mode of operation is more flexible than feeding the depleted brine to the cathode, it is more complex and requires additional pumps and auxiliary equipment.

A series of tests was carried out on the two-compartment cell with membrane separator using various cathode feed compositions. The catholyte caustic normality is determined largely by the volumetric feed rate to the cathode compartment. The cell was operated over a range of caustic normalities at three levels of sodium chloride concentration in

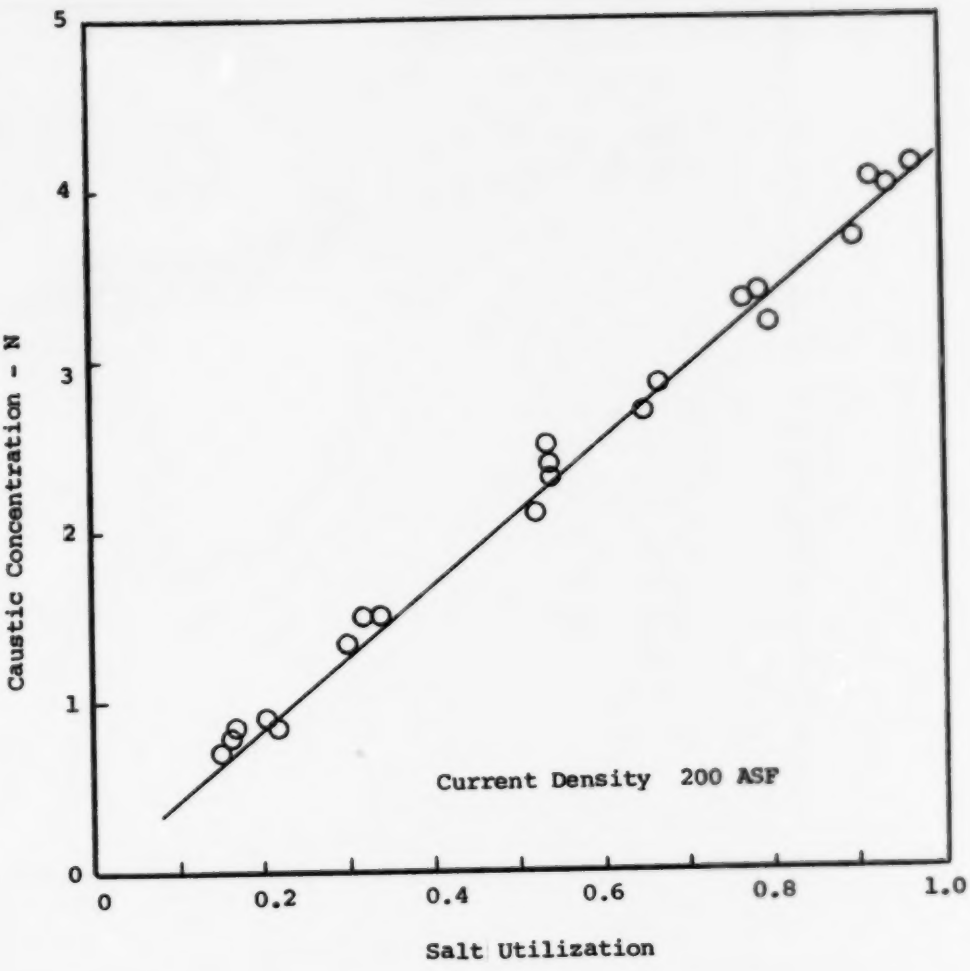

Figure 18. Dependence of Caustic Concentration on Salt Utilization for Two Compartment Cell Operated in Mode I

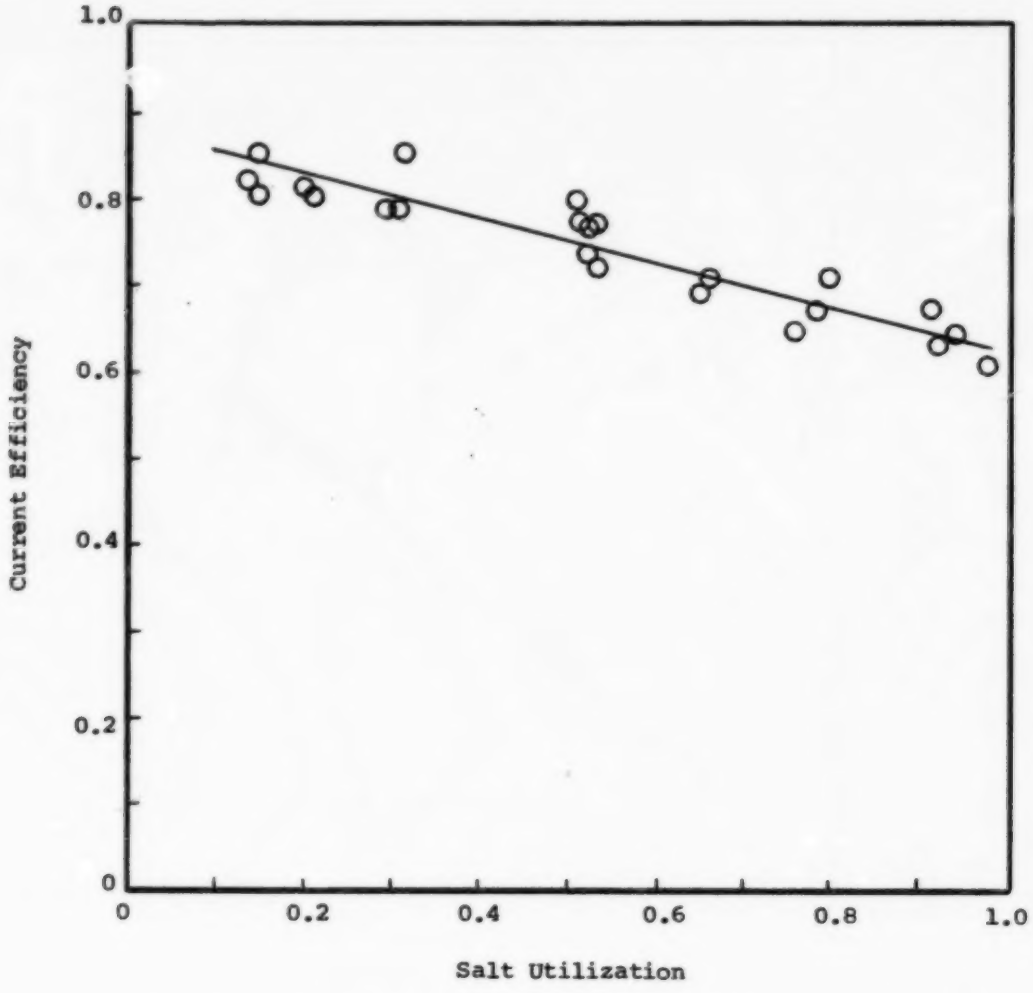

Figure 19. Dependence of Current Efficiency on Salt Utilization for Two Compartment Membrane Cell Operated in Mode I

the catholyte feed (0, 3% and 5%) and at two levels of salt utilization (50% and 90%). The purpose of these experiments was to determine the performance relationships for a cell operated in mode II and to determine the best feed composition.

The effect of salt concentration in the cathode compartment feed is shown in Figure 20. Over the range of caustic normalities from 1 to 4N, use of 3% salt feed instead of water increases the efficiency by about two percentage points and use of 5% salt feed increases it by about 6 percentage points. Since this salt is essentially unrecoverable, electric power would have to be very expensive relative to the cost of salt to justify use of salt water as an independent cathode feed.

In Figure 21 current efficiency is plotted against caustic normality for two levels of salt utilization with water feed. The current efficiency is higher for 50% salt utilization. However, this difference becomes small at 3N caustic concentration.

The same comparison is made with 5% salt feed in Figure 22. Although both curves are higher than with water feed, salt utilization has no distinguishable effect.

The relationship between cell voltage, V, and current density, i, was determined for a membrane cell with expanded metal electrodes was determined. At 75° C with water feed and caustic concentration of 2.3N this is expressed by:

$$V = 2.3 + 0.0061\ i \qquad (13)$$

Three Compartment Cell

In an attempt to combine the advantages of a membrane cell and a diaphragm cell into a single unit, the three compartment cell was designed. This is shown in Figure 17, page 40. The anode compartment is like that of the two compartment membrane cell. Brine is fed in the normal fashion and both the depleted brine and chlorine gas exit from a single port in the top of the anode compartment. Feed to the cathode is introduced into the center compartment from which it flows through a diaphragm into the cathode compartment.

This type of cell can be run in the same two modes as the two compartment membrane cell.

In mode I the anolyte liquor, separated from the chlorine gas, is fed to the center compartment. The pressure in the center compartment establishes its own level. This can be measured in a head tube which also serves to release any trapped gases from the center compartment.

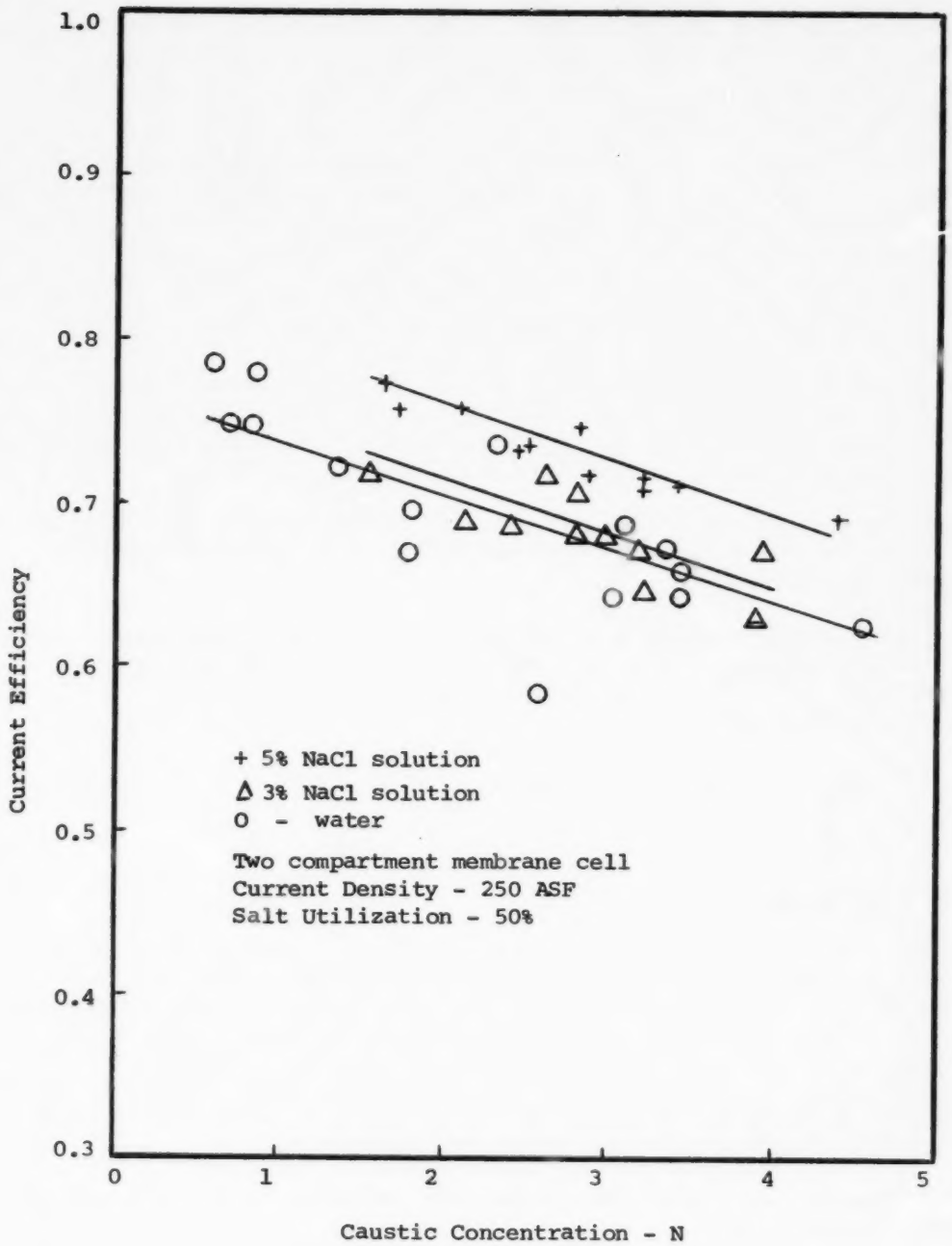

Figure 20. Effect of Salt Concentration in Cathode Feed on Cell Performance

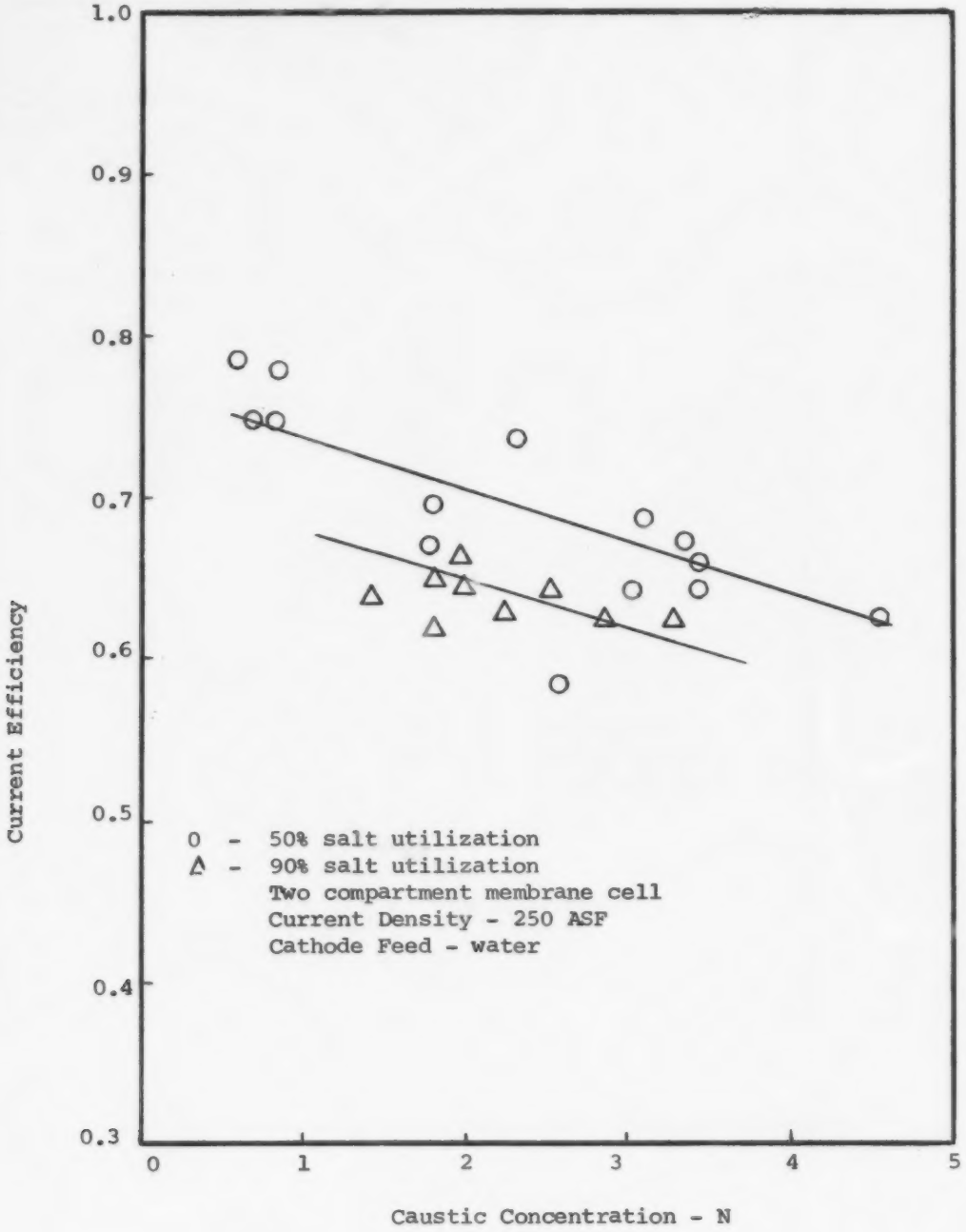

Figure 21. Effect of Salt Utilization on Cell Performance

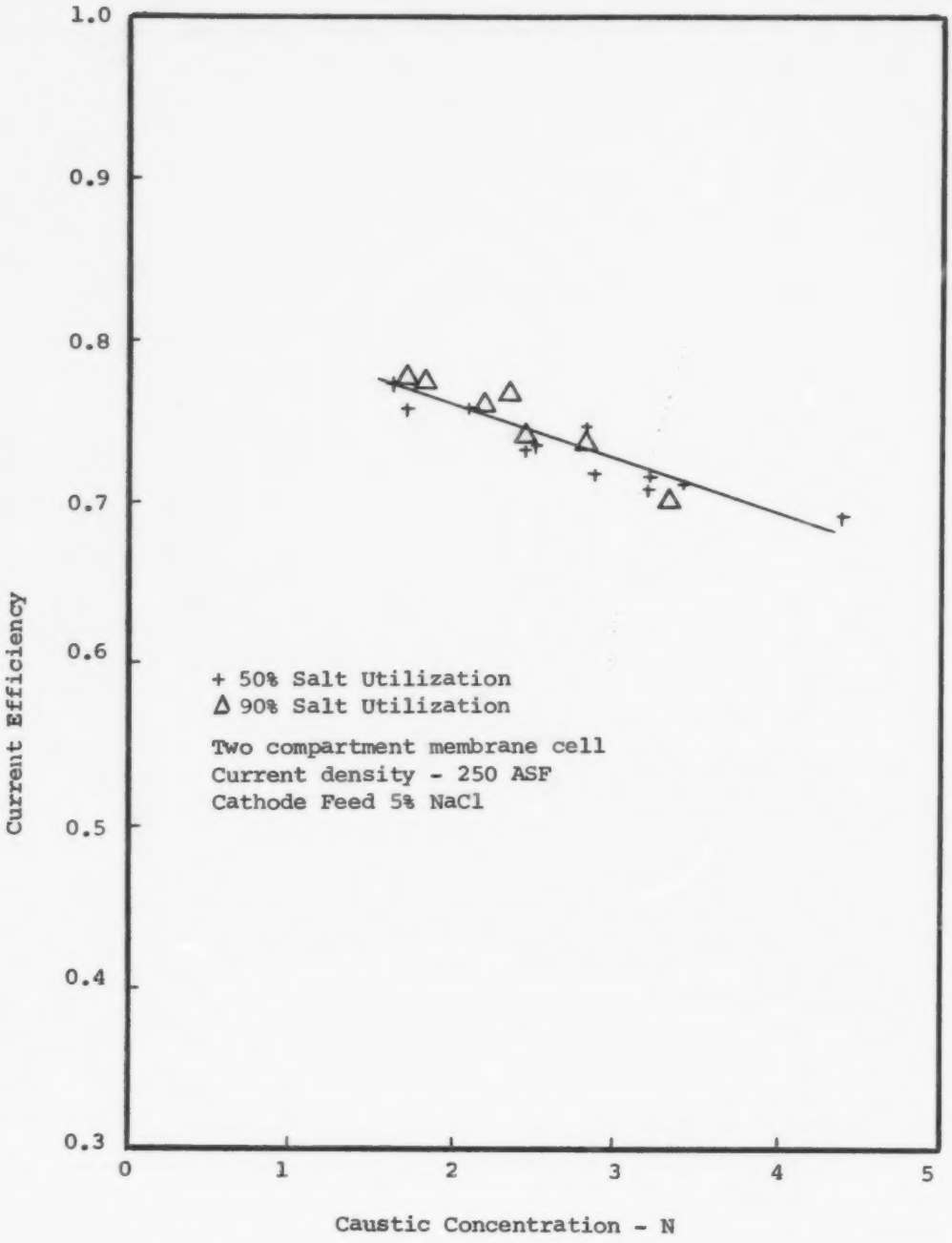

Figure 22. Effect of Salt Utilization on Cell Performance

This design combines all of the advantages of the diaphragm and membrane cells while eliminating most of their difficulties.

There are several advantages to this design. There is no need to maintain a delicate flow balance in the anode compartment. After disengagement, the anolyte liquid flows by gravity into the head tube where pressure balance is maintained by the level of the liquid. There are several resistances to back-migration of hydroxyl ions. The hydraulic flow from the center compartment to the cathode prevents the majority of hydroxyl ions from migrating into the center compartment. A large fraction of the ions that do back-migrate into the center compartment react with the dissolved chlorine in the anolyte entering the center compartment to produce hypochlorite. Consequently the hydroxyl ion concentration at the membrane is much lower than in the two-compartment cell.

The relationship between salt utilization , f, and current efficiency, η, is shown in Figure 23. This can be expressed as:

$$\eta = 0.34 \log (1-f) + 1.03 \qquad (14)$$

Comparing these results to those obtained for the two compartment cell, Figure 19, it can be seen that the current efficiency for low salt utilization is much higher with the three-compartment cell. At higher salt utilization (above $\sim$ 75%) the current efficiencies become quite similar for both cells. These results indicate that, although the three-compartment cell exhibits a significant advantage over the two-compartment cell at low salt utilization, this advantage decreases if the economics require the system operate at high salt utilization.

The relationship between voltage, V, and current density, i, for this cell is given by:

$$V = 2.3 + 0.0054\ i \qquad (15)$$

For the same current density this cell, with a 1/2 inch interelectrode spacing has a slightly higher operating voltage than the two-compartment cell.

In mode II water or dilute brine is fed to the center compartment. The advantage to this design over any other design involving a diaphragm is that the diaphragm is not exposed to chlorine gas. Consequently the diaphragm material can be selected because of the uniformity and appropriateness of its permeability rather than because of its resistance to chlorine.

The cell in this mode proved to be essentially inoperable. With water feed the cell voltage was quite high and variable. This was due to the

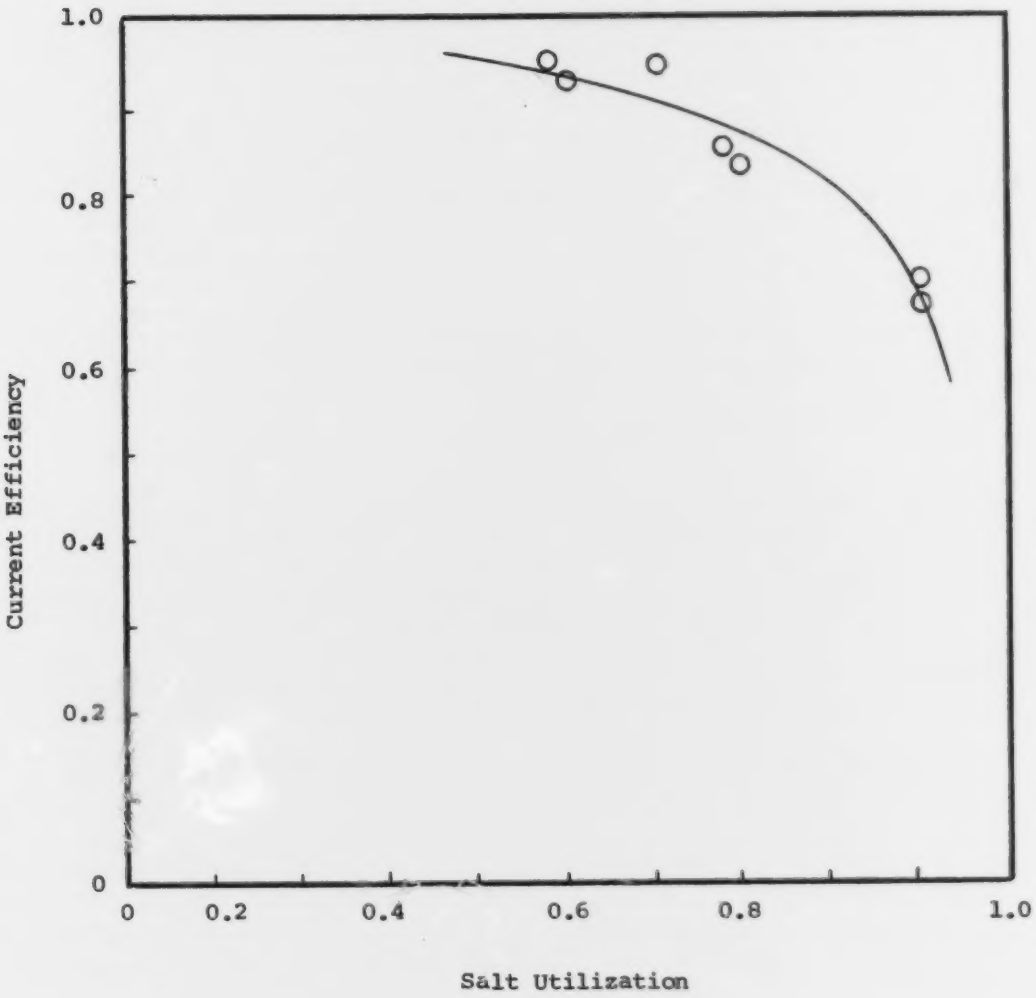

Figure 23. Dependence of Current Efficiency on Salt Utilization for Three Compartment Cell Operated in Mode I

high resistance of the center compartment which in operation contained a very dilute solution of caustic. Use of 3 or 5% sodium chloride feed reduced but did not eliminate these difficulties. No reliable operating data were obtained for this mode of operation. The difficulties experienced in the laboratory strongly suggested that the three compartment cell in mode II would not have the required reliability in the field.

Membrane Evaluation and Membrane Package Fabrication

Of the cation-exchange membranes presently available in commerce the only type which would withstand exposure to both concentrated caustic and nascent chlorine was a fluorinated membrane from DuPont. The product is designated XR for a membrane with Teflon cloth backing and R for a similar membrane without backing. (No membrane development was performed on this contract.)

Early samples of this membrane had a life-in-service of about 100 hours. These samples were of two-ply construction and the mode of failure was spalling of the resin from the membrane. Subsequent samples have been of one-ply construction. These have withstood up to 3000 hours of cumulative testing without observable changes in properties. A life-in-place of two to three years is anticipated.

This latter type of membrane was used in all membrane cells for which data are reported.

Just as it was desirable to have a packaged diaphragm for field replacement in a diaphragm cell, it is desirable to have a packaged membrane in a membrame cell. The package used at the present time consists of a fairly rigid frame surrounding the membrane. Since the membrane swells upon both heating and immersion in an aqueous solution, the membrane must be stretched prior to lamination in the frame. A special jig was made to stretch and hold the membrane during the fabrication process. Once the membrane is inserted in the jig and stretched to the desired extent, it is laminated between PVDC sheets using a special high temperature PVC resin cement.

A careful specification of membrane construction overcame a difficulty encountered with the membranes for the cell. The membranes were specified to be 24" x 24" with the active ion exchange film covering the entire surface. When the membranes were received, they were approximately one inch undersize and the edges of the film were buckled and wrinkled. It was impossible to use this membrane since the buckled edges would not allow the cell to seal properly. The membrane is a special laminate of an active film on a Teflon cloth backing, and the buckling difficulty arises from edge effects in producing large laminated areas. To resolve this problem membranes were specified

which had an active area, measured between borders of the resin fabric, only slightly larger than the active area of the cell and also had a wide border of unlaminated Teflon cloth. This design allows the membrane to be stretched in place after which the excess cloth is cut off.

Comparison of Cell Configurations

Economic analysis using the data accumulated from the small scale cell testing indicated that most economical operation would be with high saltutilization. In this light the two compartment membrane cell had a combination of advantages not possessed by any other configuration. This configuration was the simplest to fabricate, operate and maintain. The caustic concentration could be varied independently of salt utilization. This allows the cell to be run at high salt utilization with reasonable current efficiency. The membrane provides an impermeable barrier between the hydrogen and chlorine. The membrane proved to be a reliable separator that did not have to be cleaned or replaced as was the case with diaphragms. Test membranes have been run for over 3000 hours without any sign of deterioration or functional impairment. The system was simple to operate. After setting the flows to the anode and cathode compartments no further adjustments were necessary.

The current efficiency of a diaphragm cell is highly dependent upon the amount of salt that is decomposed in the cell. The relationship between current efficiency and salt utilization is shown in Figure 14. It is apparent that attempting to utilize a large portion of the salt feed results in very low current efficiencies. In industrial cells only 50% of the brine is decomposed since the efficiency drops off rapidly beyond this point.

The study of diaphragm established four significant drawbacks for th present application: poor salt utilization, difficulty of control, high maintenance and operational hazards. It is impossible to operate a diaphragm cell at a high salt utilization without suffering severe losses in current efficiency. The diaphragm cell required careful adjustments of head levels and flow rates to maintain a proper pressure balance across the diaphragm. The diaphragms tended to become fouled and plugged with time, requiring the cell to be dismantled for diaphragm replacement. Since the diaphragms were made of porous material which tended to degrade with time, a significant possibility of mixing hydrogen and chlorine existed.

The three compartment cell offered the safety and stability of a membrane cell combined with the high current efficiency of a diaphragm cell, provided it could be operated at moderate salt utilization. At high salt utilization the efficiency rapidly approached that of a two-compartment membrane cell. The internal resistance however was higher because of the greater interelectrode distance.

The most economical mode of operating the two-compartment membrane cell is with water feed to the cathode compartment. Although there is a certain increase in current efficiency when there is sodium chloride in the cathode feed, this increase in efficiency does not offset the additional salt cost. The increase in current efficiency obtained by running at a 50% versus 90% salt utilization is comparatively small. If the spent anolyte is to be discarded, the economics indicate that the high salt utilization is desirable. It might be possible to recycle the spent brine to the saturator but it is unlikely that the savings due to the increase in current efficiency would offset the additional equipment cost and complexity.

Anode Material

A number of anode materials were tested. Among them were the Englehard 3000, 7000, and 9000 grades of platinized titanium, Asahi Kasei platinized titanium, resin impregnated graphite, and Electrode Corp. DSA electrodes.

The anode potentials determined in the laboratory are shown in Table 5 for these materials. A Luggin capillary was inserted in the cell and the tip placed within one tip diameter of the electrode surface. The potential between the working electrode and a saturated calomel electrode was measured with a high impedance vacuum true voltmeter. The electrode with the lowest operating voltage was the expanded DSA electrode. The expanded electrode allows the Luggin capillary to be inserted from the back so it does not interfere with the current flow within the cell. The measurement of voltage of the other electrodes may be slightly influenced by the presence of the Luggin capillary but only by a few millivolts at most.

These comparative tests were not run for long enough to provide any information about aging characteristics except that the graphite was observed to ablate or spall at current densities above 150 ASF. The usable lifetime of the DSA electrodes can be assumed to be about 5 years based on their use under similar conditions in the chlorine industry.

Cathode Material

Six materials were evaluated as cathodes. These were Hastelloy C, Monel 400, 316 stainless steel, Inconel 625, nickel 200 and mild steel. The cathode potentials of these materials at various current densities are shown in Table 6. The voltages shown are referred to a saturated calomel reference electrode and the method of test is similar to that used for anodes described above.

Table 5

Comparison of Anode Operating Potential (Volts)*

Current Density (ASF)	Platinized Titanium (Englehard Incl.) Series 3000	Platinized Titanium (Englehard Incl.) Series 2000	Platinized Titanium (Englehard Incl.) Series 9000	Platinized Titanium (Asahi)	Resin Impregnated Graphite	DSA on Expanded Titanium (Electrode Corp.)
200	1.85 (38°C)	1.85 (38°C)	1.75 (38°C)	1.85 (38°C)	2.25 (40°C)	1.00 (48°C)
300	1.85 (45°C)	1.95 (39°C)	1.85 (44°C)	2.00 (44°C)	2.50 (46°C)	1.00 (53°C)
400	1.90 (53°C)	2.00 (43°C)	1.95 (50°C)	2.10 (51°C)	-	1.00 (65°C)
500	1.95 (58°C)	-	-	2.20 (58°C)	-	-

* Measured against saturated calomel reference electrode

Table 6

Comparison of Cathode Operating Potential (Volts)*

Current Density ASP	Stainless Steel 316	Hastalloy C	Monel Alloy 44	Nickel 200	Inconel 625	Mild Steel
200	1.80 (39°C)	1.55 (38°C)	1.65 (38°C)	1.50 (35°C)	1.50 (39°C)	-
300	1.95 (45°C)	1.50 (45°C)	1.80 (45°C)	-	-	1.65 (45°C)
400	2.10 (48°C)	1.75 (40°C)	1.95 (50°C)	1.60 (56°C)	1.60 (44°C)	-
500	2.20 (55°C)	-	-	-	-	-

* Measured against saturated calomel reference electrode

Unlike the selection of anodes, there was no obvious choice for cathode material. Hastelloy, Inconel and nickel have the lowest potentials but only by small fractions of a volt. Intermittent cell operation causes the cell to be inactive for long periods of time during which time the cathode is exposed to highly oxidative species. Hastelloy C has the best corrosion resistance. However it is expensive and difficult to fabricate. If the cell were to have sheet cathodes, Hastelloy C might well be used. However, for an expanded cathode it is a less desirable choice. The other materials would all require a trickle current for cathode protection during the periods that the cell was not active. After provision is made for a trickle current, then the advantage lies with the cheapest material. The final decision to use mild steel cathodes was probably strongly influenced by the fact that the chlorine industry has found that mild steel provides the lowest cost cathodes.

Gasketing Material

A gasket, in the form of a flat gasket, is used as a seal between each of the compartments in the cell. Several different gasketing materials have been evaluated for use in the anolyte section of the cell. This compartment provides the most corrosive atmosphere. Tygon, butyl rubber, silicone rubber, and Viton all exhibited severe attack by the corrosive environment. Teflon exhibits no attack or swelling, however it is fairly rigid and is subject to cold flow. Neoprene appears to undergo a superficial attack on exposed surfaces but this is not progressive. Neoprene gaskets have been in intermittent service for at least 6 months. Ethylene propylene rubber (EPR) is claimed to have superior chlorine resistance. This material appears satisfactory based on testing over several months. This material appears satisfactory based on testing over several months. EPR was selected as the anode gasket material with neoprene as an alternative.

In industrial practice butyl rubber has shown exception resistance to caustic attack. This material has been successfully in the cathode compartment. However, to prevent the possibility of gaskets being interchanged during cell assembly, the anode gasketing material will be used in the cathode compartments.

Full Scale Unit Design and Performance

After determining the most favorable cell configuration, a single full scale cell was built and tested. The full scale cell had an active area of 2.2 square feet. The cell compartments were constructed from high temperature PVC which had shown in tests to have satisfactory resistance to wet chlorine. The full scale cell and test rig appear in Figure 24.

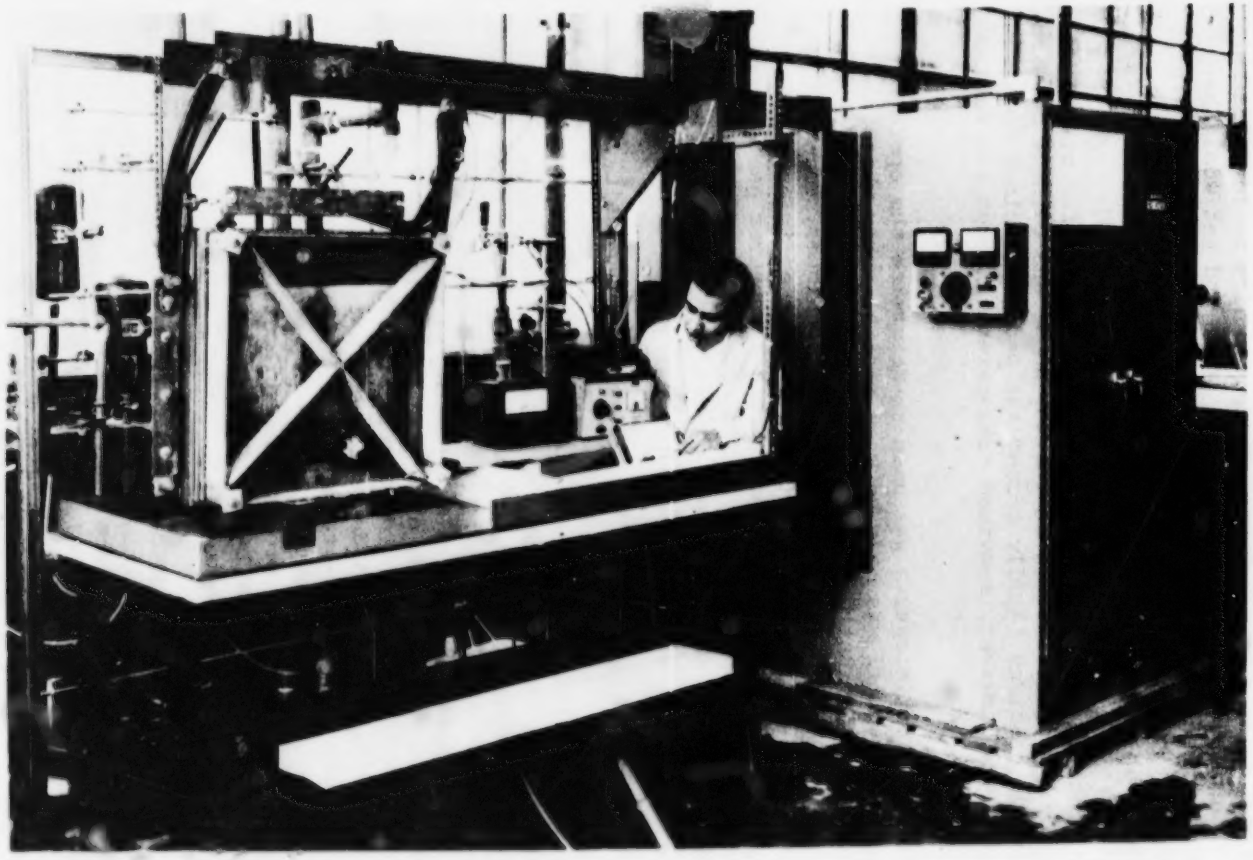

Figure 24. Two Cell Stack and Associated Test Apparatus

For the full scale cell, end plates were designed which would distribute the sealing pressure evenly over the gasketed areas and yet would be light in weight. These were fabricated from 1/4" by 3" stainless steel stock with the short dimension against the end block. The end plate design can be seen in Figure 24.

End blocks were constructed from 1" thick lucite to allow for visual inspection of gas release and foaming inside the anode and cathode compartments. Exposure to chlorine rapidly turned the anode end block opaque. The cathode end block, however, remained transparent through the testing of this cell.

A fairly conventional optimization was used to determine the operating current density. A tradeoff was made between capital costs which decrease with increasing current density, and power costs, which increase with increasing current density. With computer techniques, second order effects like the effect of current density on current efficiency and discontinuous functions like electric power rate structures can be considered in this optimization. For the design case the optimum current density was approximately 240 amperes per square feet (ASF) and the cost-current density curve was quite shallow.

In this cell heat build-up can affect operating current density. The energy which corresponds to the excess of operating voltage over 2.15 volts is converted into heat. The energy which relates to the 2.15 volts is converted into chemical energy of reaction. Since the quantity of brine fed to the anode compartment is constrained by the necessity of obtaining high salt utilization and the quantity of water fed to the cathode compartment is limited by the requirement of producing a concentrated hypochlorite solution, the operating temperature of the cell shows a steady increase with current density. Since high temperature produces high conductivity, this is desirable but not to the point that the electrolyte boils. A desirable temperature is 85 to 90^{o} C. With 85% salt utilization, a current density of 240 ASF produces an operating temperature of 88^{o} C. With other economic constraints it is possible that the current density should be held below the economic optimum to avoid too high a cell temperature.

The current efficiency of the large cell was found to be higher than that of the small cells (80% vs 65%). This was confirmed by a large amount of operating data near 240 ASF. Since there is no external circulation, essentially all convection past the electrode and membrane surfaces is due to internal gas-lift recirculation. This is improved both by increasing the height of the electrode and increasing the depth of the compartment. Both the anode and the membrane can be affected by polarization layers and it is not clear at this time whether one or both are affected.

Analysis showed that the salt utilization has little effect on either cell voltage or current efficiency. The cell voltage decreases slightly

as the salt cut is increased because the temperature rises as the brine flow role is lowered. There is simultaneously a slight increase in the current efficiency since less dissolved chlorine is carried out by the anolyte.

Varying the water feed to the cathode has a more significant effect than varying the brine feed. As the amount of water fed to the cathode is decreased the caustic concentration is increased. The higher hydroxyl ion concentration causes a greater back migration across the membrane which decreases the cell efficiency. This relationship is shown in the table below.

Table 7

Effect of Varying Water Feed to Cathode

NaOH Normality	NaOCl Normality	% System Efficiency	Cell Voltage	Temp °C
2.00	1.83	77	3.83	86
2.75	2.50	72	3.65	90

The cell voltage is lower in the case of the higher caustic concentration. This decrease in voltage is due to the increased temperature and the more conductive catholyte.

Since it is desirable to utilize at least 80% of the salt feed, the present limits of caustic concentration are between 2.00N and 2.85N. The lower limit is economic in nature since, as the concentration of the hypochlorite solution decreases storage and handling costs increase rapidly. The upper limit is presently set by the heating effects in the cell stack. Several methods of cooling are presently being considered which may allow the production of more concentrated sodium hypochlorite.

The next step in the development program was the design and testing of a two cell stack. The two cell stack was used to test and evaluate methods of electrical connection and hydraulic manifolding of the cells. It was clearly desirable to have a series-connected cell stack. There are several alternative means of internal connection. Leading the current out of each cell is expensive, wasteful of power and conducive to leaks. Bipolar sheet electrodes are ideal from the standpoint of electrical connection, but the operating cell voltage is much higher because of the increased inter-electrode spacing. The solution selected was to weld circular lugs on the back of each electrodes. These are connected through the cell walls. For the 16" by 20" electrode, two lugs were used.

Current efficiency of the two cell stack was found to be essentially the same as that of the single large cell. The voltage per cell, V, at 60° C is related to current density, i, by:

$$V = 2.4 + 0.00595\ i \qquad (16)$$

The slope of this curve decreases slightly with temperature.

Effect of Calcium and Magnesium

All commercially available sodium chloride contains some calcium (Ca) and magnesium (Mg) salts as naturally occurring impurities. Further, although usually smaller, quantities of these materials are introduced into the brine through the feed water. In the electrochemical cell these impurities can cause difficulties by formation of insoluble hydroxides. A diaphragm cell is most sensitive because the precipitates tend to plug the diaphragm. However, difficulties can occur because of scale formation on membrane and electrode surfaces. In general cheaper grades of salt contain more impurities. This problem was only given a cursory examination during the present program. The decision was made to use quite pure salt at the Somerville installation despite its higher cost to avoid operating difficulties. Further research is needed to determine what concentrations of calcium and magnesium, and of sulfate can be tolerated in the feeds to the hypochlorite generator and what means of pretreatment would be practical.

Brine prepared from rock salt contains between 150 and 300 ppm of Ca^{++} and 0-50 ppm of Mg^{++} . Brine from food grade salt usually contains 5-25 ppm of Ca^{++} and 0.5 ppm of Mg^{++} . Experimentally some difficulty was encountered with fouling of the diaphragms because of the presence of calcium and magnesium. After several weeks of operation the three compartment cells showed a gradual rise in the pressure drop across the diaphragms. When the cells were disassembled, a white gelantinous precipitate was found on the center compartment side of the diaphragm. Analysis of this residue showed it to be primarily calcium and magnesium hydroxides. Although food grade salt was used to prepare this brine, the pH of the center compartment was sufficient to form precipitates.

One method of pretreatment is the injection of sodium carbonate and sodium hydroxide into the brine saturator. These additives cause the precipitation of calcium as calcium carbonate and magnesium as magnesium hydroxide. The solubility products of these two components are:

$$[Mg^{++}] \times [OH^-]^2 = 1.2 \times 10^{-11} \qquad (18^\circ\ C) \qquad (17)$$

$$[Ca^{++}] \times [CO_3] = 0.8 \times 10^{-8} \qquad (25^\circ\ C) \qquad (18)$$

Thus if the solution in the lixator is made .01N in each of hydroxide (OH^-) and carbonate ($CO_3^=$) the equilibrium concentrations of calcium and magnesium would both be below 1 ppm.

A study was performed to determine the efficacy of this brine treatment procedure. Three samples of brine were prepared, the first using rock salt, the second using rock salt treated with one gram per liter of both sodium hydroxide and sodium carbonate, and the third using food grade salt. The results are shown in Table 8.

Table 8

Comparison of Brine from Three Grades of Salt with Pretreated Brine

	ppm Ca^{++}	ppm Mg^{++}
Untreated rock salt	195	3
Treated rock salt	16	0.2
Food grade salt	14	0
Pretreated brine	< 5	< 1

It can be seen that the treatment method effects over a tenfold improvement in hardness and produces a brine somewhat better than that obtained with food grade salt. The practicability of this or similar treatment on a large scale has not been investigated.

Reactor Development

In the reaction of caustic with chlorine:

$$2\ NaOH + Cl_2 \rightarrow NaCl + NaOCl + H_2O \qquad (19)$$

to form hypochlorite, a slight excess of caustic must be maintained. If the reaction is allowed to proceed in an acid environment, caused by an excess of chlorine, the following reactions occur.(5)

$$Cl_2 + H_2O \rightarrow HOCl + Cl^- + H^+ \qquad (20)$$

$$HOCl \rightleftarrows OCl^- + H^+ \qquad (21)$$

$$2HOCl + OCl^- \rightarrow ClO_3^- + 2Cl^- + 2H^+ \qquad (22)$$

The rate of reaction (22) is very sensitive to pH. Since this reaction converts a weak acid (HOCl) to a strong acid (HCl), the sequence is autocatalytic and can produce boiling with the release of oxygen, HCl gas and chlorine. It also converts hypochlorite to chlorate. Sodium chlorate ($NaClO_3$) is very stable and is useless for disinfection. Thus, it is essential to avoid over-chlorination and the inherent problems that are associated with it.

The need to avoid over-chlorination requires use of a concurrent reactor rather than a counter-current reactor. In a counter-current reactor the nearly neutral hypochlorite at product concentration would encounter a large stream of entering chlorine. The stream would rapidly become acidic producing localized over-chlorination. In the co-current mode as the hypochlorite becomes more concentrated and as the pH of the stream decreases, the chlorine is depleted.

The product hypochlorite exits from the reactor through a side-arm via gravity overflow. Any inerts in the gas stream are vented through the top. The gravity overflow design offers a simple method of flow control which avoids the need for level controllers or flow regulators. The reactor constructed in this manner is capable of operating over a wide range in flow rates without the necessity of changing any control settings.

In the design of the reactor, consideration must be given to removal of the heat of reaction. The heat of reaction of chlorine with caustic is about 600 BTU per pound of chlorine. Since the rate of chlorate formation increases with increasing temperature, it is necessary to cool the reactor to suppress this reaction. Production of 10% hypochlorite would be accompanied by a 60° F rise in temperature without cooling. Production of 5% hypochlorite would cause a 30° F rise. The cooling can be most easily accomplished by circulating cooling water through a titanium tubing coil incorporated in the reactor.

Inefficiencies in the cell actually help avoid the possibility of chlorate formation in the reactor. Generation of caustic at the cathode is essentially stoichiometric. The anode under any conditions generates some chlorine and some chlorine is lost by solution in the spent brine stream. Consequently there is always a small but useful excess of caustic over chlorine in the cell products. This will help ensure the stability of a well-run reactor.

Initial tests were conducted with a tall, narrow packed bed reactor. Co-current upflow design performed very well. The glass helices used for packing gave very good liquid-vapor contact with essentially no unreacted chlorine gas escaping with the inerts. There is also no evidence of channeling or localized over-reaction.

The column run without cooling confirmed the temperature rise calculations. In the initial studies the temperature of the starting reactants was

approximately 25° C and the product had a temperature of between 55° - 60° C. In the actual production unit where the reactants are fed to the reactor at a temperature in the area of 70° C cooling will be necessary. Above 80° C chlorate formation becomes quite significant.

Several additional runs with using the small scale lab reactor produced varying results. The reaction efficiency ranged between 50% to 90% with product temperatures ranging between 45° to 80° C of a feed temperature of 23° C. The high temperatures were caused by over-chlorination which also accounts for the poor reaction efficiency of some of the runs.

In order to control the temperature an internal cooling coil for the reactor was fabricated from 1/4" titanium tubing.

Since the reaction is quite rapid, good gas-liquid contact is not extremely important. The design consisting of a titanium coil in an annular space described in Section II was selected in preference to the packed bed because of its relative simplicity.

Hydrogen Disposal

For a chlorine production rate of 15 lb/hr, 1.6 cubic feet per minute of hydrogen is produced. Although this flow is quite small it is desirable to provide a safe means of disposing of the hydrogen to eliminate the possibility of fire or explosion. After considering various methods of disposal it was decided that the easiest and most efficient way to dispose of the hydrogen would be to vent it into a duct where it would be diluted with a large volume of air and exhausted to the outside. Hydrogen in air has an upper explosive limit of 74.2 volume percent and a lower explosive limit of 4.0 volume percent. (4) Allowing a safety factor of three, a hydrogen concentration of 1.3% in the duct would require 150 CFM of air. In a four inch diameter duct, this flow produces a velocity of about 30 feet per second with an essentially negligible pressure drop. The resulting Reynolds number is 64,000 ensuring turbulent flow and thorough mixing of the hydrogen with air. This system requires a small blower installed in the duct vented to the outside. A safety interlock automatically shuts down the cell if the fan were to fail.

SECTION IV

SYSTEM OPTIMIZATION

The basis for optimization of the hypochlorite generator is minimum total cost to the user. A computer program was developed to permit the optimization of operating variables, like salt utilization and current density for a particular cell configuration and for specific economic inputs. The program, as presented in Figure 25, applies to a diaphragm cell with economic inputs suitable to the Boston University Bridge site. Use of this program for other cell configurations requires that the appropriate internal relationships, given in Section III, be used. Economic inputs which depend on location are indicated with a dagger (†) at the end of the line, which is not part of the program. The program is written in Fortran IV for GE400 timesharing. Other systems should require at most modification of the input and output statements.

In this program the chlorine production rate, J, is expressed in theoretical amperes, that is, the current which would be required if the generation process were 100% efficient. Values are assumed for the independent variables, salt utilization and current density. Capital equipment costs (cells, rectifier, brine storage tank, pumps and cell cooling, if required) are calculated. These are multiplied by the capital amortization factor, F:

$$F = \frac{I}{1 - (1 + I)^{-N}} \qquad (23)$$

which depends upon the interest rate, I, and the number of amortization periods, N. Provision is made for amotizing the cells, which are likely to have a shorter lifetime than the other equipment, over a different amortization period. The equations used are listed in Table 9. When these quantities are summed and multiplied by an industrial mark up factor (1.7 was used) the result is the cost per year of owning the equipment. Annual operating costs (salt, energy, electrical power demand charge and water) are calculated by the equations in Table 10. The nomenclature for these equations and the computer symbols used are listed in Table 11. Total annual cost is the sum of amortized capital costs and operating costs.

The program stores the results of the first calculation, increments the independent variables separately and recalculates. If a new set of independent variables gives a lower annual cost than the stored value, the old results are replaced by the new results.

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Figure 25. Hypochlorinator Optimization Program

```
      REAL INT,NC,NR,M,KWM,K,KW,KWCHS,KWHR
      K=.00482
      INT=.07
      NR=30.
      NC=30.
      ANHR=240.          †
      PUMS=3.
      ENRS=1.
      COOLSP=1.
      DEMCH=1.
      DOSE=4.3           †
      OFLOW=90.          †
      SALS=.022
      Q=6.
      DF=1.2
      SELFAC=1.7
      CELS=120.
      M=.003
      V=2.4
      FOD=.1
      FOYSTR=0.
      FM=1.
      KWM=1.
      CDM=1.
      FT2M=1.
      ANCOSM=10E10
C
C     COMPUTATION OF SEVERAL VARIABLES INDEPENDENT OF
C     THE DO-LOOP
C
      ANHRS=ANHR/FOD
      DESCAP=118.98*DOSE*OFLOW**FOD
      RNC=-NC
      AMC=INT/(1.-(1.+INT)**RNC)
      RNR=-NR
      AMR=INT/(1.-(1.+INT)**RNR)
      DD=DF*DESCAP
C
C
C     THIS IS THE BEGINNING OF THE DO-LOOP TO DETERMINE THE
C     MINIMUM ANNUAL COST.  ALL PARAMETERS DEFINED IN THE
C     DO-LOOP ARE DEPENDENT ON THE VALUES OF CD AND/OR F.
C
C
      DO 1, I=1,10
      II=I*50
      DO 2, J=5,9
      RJ=J
      RJ=RJ/10.
      CD=II
```

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Figure 25. (Continued)

```
      F=RJ
   40 CONTINUE
      CE=.146*ALOG(1.-F)+1.01
      CEL=(DD*CELS*AMC)/CD/CE
      KW=DD*(M*CD+V)/(1000.*CE)
      REC=(KW/40.)**.67*1340.*AMR
      REC=2.*REC
      FT2=DD*100./(100.*CE*CD)
      ROKSAL=ANHRS*K*DD/Q/F
      IF(ROKSAL.GT.20000.) GO TO 50
      BRSTR=(ROKSAL/10000.)**.37*1900.*AMR
      GO TO 51
   50 BRSTR=(3800*(ROKSAL/20000.)**.355+1500.)*AMR
   51 PUM=DD/F*K*PUMS*AMR
      HYT=((DESCAP*K*ANHRS*FOYSTR)**0.59)*10.9*AMC
      SALT=DESCAP/F*K*ANHRS*SALS
C
C
C        THE FOLLOWING IF STATEMENTS CALCULATE THE
C        ELECTRICAL DEMAND CHARGE AND THE COST OF
C        ENERGY FOR THE HYPOCHLORINATOR.
C
C
      IF(DEMCH.EQ.0.) GO TO 52
      IF(KW.LE.20.) GO TO 53                              †
      IF(KW.GT.20..AND.KW.LE.70.) GO TO 54                †
      IF(KW.GT.70..AND.KW.LE.500.) GO TO 55
      PRINT 99
   99 FORMAT( "  KW>500  ")
      GO TO 55
   53 DEMCS=0.
      GO TO 52
   54 DEMCS=2.9*12.*(KW-20.)
      GO TO 52
   55 DEMCS=(2.6*(KW-70.)+2.9*50.)*12.
   52 LABOR=(DESCAP/5000.)**.2*AMR*2500.
      KWHR=KW*ANHR/(FOD*12.)
      IF(KWHR.LE.800.) GO TO 60                           †
      IF(KWHR.GT.800..AND.KWHR.LE.1200.) GO TO 61         †
      IF(KWHR.GT.1200..AND.KWHR.LE.4000.) GO TO 62        †
      IF(KWHR.GT.4000..AND.KWHR.LE.20000.)GO TO 63        †
      IF(KWHR.GT.20000..AND.KWHR.LE.120000.)GO TO 863     †
      IF(KWHR.GT.120000.) GO TO 865                       †
   60 KWHCS=KWHR*.059
      GO TO 64
   61 KWHCS=800.*.059+(KWHR-800.)*.05
      GO TO 64
   62 KWHCS=800.*.059+.05*400.+.0275*(KWHR-1200.)
      GO TO 64
   63 KWHCS=800.*.059+20.+2[illegible]00.*.0275+(KWHR-4000.)*.016
```

Figure 25. (Continued)

```
 GO TO 64
 863 KWHCS=400.2+(KWHR-20000)*.012
 GO TO 64
 865 KWHCS=1600.2+(KWHR-120000.)*.0097
 GO TO 64
 64 ENERG=DEMCS+KWHCS*12.
 IF(CD.LE.250.) GO TO 70
 WATER=(1.1E-6*CD**2+CD*1.4E-4-.11)*FT2*DF
 IF(WATER.GT.22.) GO TO 71
 COOL1=(FT2*COOLSP+78.)*AMR
 COOL2=(FT2*COOLSP+270.)*AMR
 GO TO 72
 71 COOL1=(FT2*COOLSP+11.6*WATER**.495)*AMR
 COOL2=(FT2*COOLSP+40.2*WATER**.495)*AMR
 72 WAT=WATER*7.2E-05*ANHRS                    †
 A1=COOL1*SELFAC+WAT
 A2=COOL2*SELFAC
 IF(A1.LT.A2) GO TO 73
 WAT=0.
 COOL1=0.
 GO TO 80
 70 COOL1=0.
 WAT=0.
 73 COOL2=0.
 IF(FOD.LT.1.) GO TO 81
 80 ANCO1=(CEL+REC+BRSTR+PUM+COOL1+COOL2)*SELFAC+SALT+ENERG+
&WAT
 ANCOS=ANCO1+LABOR*SELFAC
 GO TO 82
 81 ANCO1=(CEL+REC+BRSTR+2.*PUM+COOL1+COOL2+HYT)*SELFAC+
&SALT+ENERG+WAT
C
C
C       THE MINIMUM ANNUAL COST OF OPERATION IS
C       DETERMINED BY RETAINING MINIMUM VALUES OF:
C       F,CD,KW,FT2 AND ANCOS AS THE PROGRAM GOES
C       THROUGH THE ITERATIONS IN THE DO-LOOP.
C
C
 ANCOS=ANCO1+LABOR*SELFAC
 1202 FORMAT(5X,F4.3,5X,F5.0,5X,F8.2)
 82 IF(ANCOS.GE.ANCOSM) GO TO 90
 ENERGM=ENERG
 SALTM=SALT
 CELM=CEL
 RECM=REC
 CEM=CE
 FM=F
 CDM=CD
 KWM=KW
```

Figure 25. (Continued)

```
 FT2M=FT2
 ANCOSM=ANCOS
 90 CONTINUE
 2 CONTINUE
 1 CONTINUE
 PRINT 100
 100 FORMAT(////,6X,"F",6X,"CD",8X,"MINANCOST",8X,"KW",6X,
&"FT2",//)
 PRINT 101,FM,CDM,ANCOSM,KWM,FT2M
 101 FORMAT(F9.2,F8.1,5X,F9.1,F12.1,F10.2,//)
 CLCOST=ANCOSM/(DOSE*ANHR*OFLOW*8.33/24.)
 PRINT 102,CLCOST
 TCEL=CELM/AMC
 102 FORMAT(" THE COST OF GENERATED CL IS",F6.3," $/LB",/)
 103 FORMAT(3X,"THE ANNUAL ENERGY COST IS  $",F8.2)
 104 FORMAT(3X,"THE ANNUAL SALT COST IS  $",F8.2)
 105 FORMAT(3X,"THE TOTAL CELL COST IS  $",F8.2)
 106 FORMAT(3X,"THE TOTAL RECTIFIER COST IS  $",F8.2)
 107 FORMAT(3X,"CELL COST-$/YR=",F8.2,3X,"RECT COST-$/YR=",F8.2)
 PRINT 103,ENERGM
 PRINT 104,SALTM
 PRINT 107,CELM,RECM
 TREC=RECM/AMR
 PRINT 105,TCEL
 PRINT 106,TREC
 CAPCOS=(ANCOSM-ENERGM-SALTM-WATM)/AMR
 108 FORMAT(3X,"TOTAL CAPITAL EQUIPMENT COST IS  $",F8.2)
 PRINT 108,CAPCOS
  109 FORMAT (3X,"PERCENT CURRENT  EFFICIENCY=",F3.0)
 CEM=CEM*100.
 PRINT 109,CEM
 95 CONTINUE
 END
```

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Table 9

Amortized Capital Equipment Costs

Cells: $$A_c = \frac{J \cdot D \cdot C_c \cdot F_c}{i \cdot \eta}$$

Rectifier: $$A_r = \frac{1340\ P^{0.67} \cdot F_r}{40}$$

Brine Storage Tank: $$A_b = \frac{1900\ V_s^{0.37} \cdot F_r}{10{,}000}$$

$$A_b^{*} = \left(\frac{3800\ V_s^{0.355}}{20{,}000} + 1500 \right) F_r$$

Pumps: $$A_p = \frac{J \cdot D \cdot k_s \cdot C_p \cdot F_r}{f}$$

Cooling Spacers: $$A_m^{**} = \left(\frac{J \cdot D \cdot C_s}{i \cdot \eta} + 78 \right) F_r$$

$$A_u^{**} = \left(\frac{J \cdot D \cdot C_s}{i \cdot \eta} + 270 \right) F_r$$

SUPPORTING EQUATIONS

$$P = \frac{J \cdot D\ (V_o + iR)}{1000\ \eta}$$

$$V_s = \frac{J \cdot D \cdot t_r \cdot k_s}{N_d \cdot f}$$

$$\eta = 1.01 + 0.146 \ln (1-f)$$

* If more than 2000 lbs of salt is to be stored.

** The cost of using municipal water is compared to that of using runoff. The lower total cost alternative is selected.

Table 10

Annual Operating Costs

Salt: $$A_s = \frac{J \cdot k_s \cdot t_r \cdot C_1}{f}$$

Energy: $$A_e = \frac{J \cdot t_r \cdot C_e (V_o + iR)}{1000}$$

Demand Charge: $$A_d = C_d \cdot P$$

Water: $$A_w = 7.2 \times 10^{-3} \, W \cdot t_r$$

SUPPORTING EQUATION:

$$W = \frac{(1.18 \times 10^{-6} i^2 + 1.4 \times 10^{-4} \, i - 0.11) \, J \cdot D^2}{i \cdot \eta}$$

Table 11

Nomenclature Used in Economic Analysis

Symbol	Computer Designation	Significance
A_b	BRSTR	Amortized Brine Storage Cost, $/year
A_c	CEL	Amortized Cell Cost, $/year
A_d	DEMCS	Kilowatt Demand Charge, $/year
A_e	KWHCS	Energy Cost, $/year
A_m	COOL1	Amortized Cost for Cell Cooling Using Municipal Water, $/year
A_p	PUM	Amortized Brine Feed Pump Cost, $/year
A_r	REC	Amortized Rectifier Cost, $/year
A_s	SALT	Salt Cost, $/year
A_u	COOL2	Amortized Cost for Cell Cooling Using Runoff, $/year
A_w	WAT	Cost of Municipal Water for Cooling, $/year
C_c	CELS	Factory Cost of Cells, $/ft^2
C_d	DEMCH	Demand Charge, $/kilowatt
C_e	ENRS	Electrical Energy Price, $/kilowatt hour
C_l	SALS	Salt Price, $/lb
C_p	PUMS	Cost of Brine Feed Pump, $/lb salt hr^{-1}
C_s	COOLSP	Factory Cost of Cooling Spacers, $/ft^2
D	DF	Design Contingency Factor
F_c	AMC	Amortization Factor for Cells, year^{-1}
F_r	AMR	Amortization Factor for Other Equipment, year^{-1}
f	F	Salt Utilization, expressed as decimal
i	CD	Current Density, amps/ft^2
J	DESCAP	Rate of Usable Chlorine Production, theoretical amperes
k_s	K	Conversion Factor, 0.00482 lb NaCl/ampere hour
N_d	Q	Number of Salt Deliveries per year
P	KW	Power Rating of Rectifier, kilowatts
R	M	Effective Internal Resistance of Cell, ohm-ft^2
t_r	ANHRS	Fraction of Time in Operation, hrs/year
V_o	V	Extrapolated Zero-Current Cell Voltage, volts
V_s	ROKSAL	Salt Storage Capacity, lbs of salt
$\dot{w}$	WATER	Cooling Water Required, gals/ft^2
η	CE	Current Efficiency, expressed as decimal

The costs of operating labor and some capital equipment like the press that holds the cells do not appear in this calculation. These are not strong functions of the independent variables and do not affect the optimization.

An example of the use of this program is shown in Figure 26. This was the result of a paper study of the use of the hypochlorite generator at the Boston University Bridge Facility. The assumption was first made that the unit would operate only during storm overflow conditions (Point 1). In this application, since the power required for pumping during overflow conditions is very much more than the power demand of the cells, the hypochlorite generator does not carry a demand charge if it is not operating during the storm. This mode of operation (Points 2 to 6) does require product storage tanks which on an amortized basis cost much less than the demand charge. In this mode the ratio of production rate to consumption rate becomes a third independent variable. This is used as the abscissa in the figure. To give an indication of how the operating variables are related, the conditions at optimum are given for the various points calculated. For reference at this installation an average overflow of 100 MGD is expected for 300 hours per year. The dosage rate is 3 ppm. The quoted treatment cost does not include estimated fixed costs of $700 per year which amounts to 0.056¢/Kgal. The treatment cost with electrochemically generated hypochlorite can be compared to that using truck-delivered solution which was estimated at 0.7¢/Kgal at this location

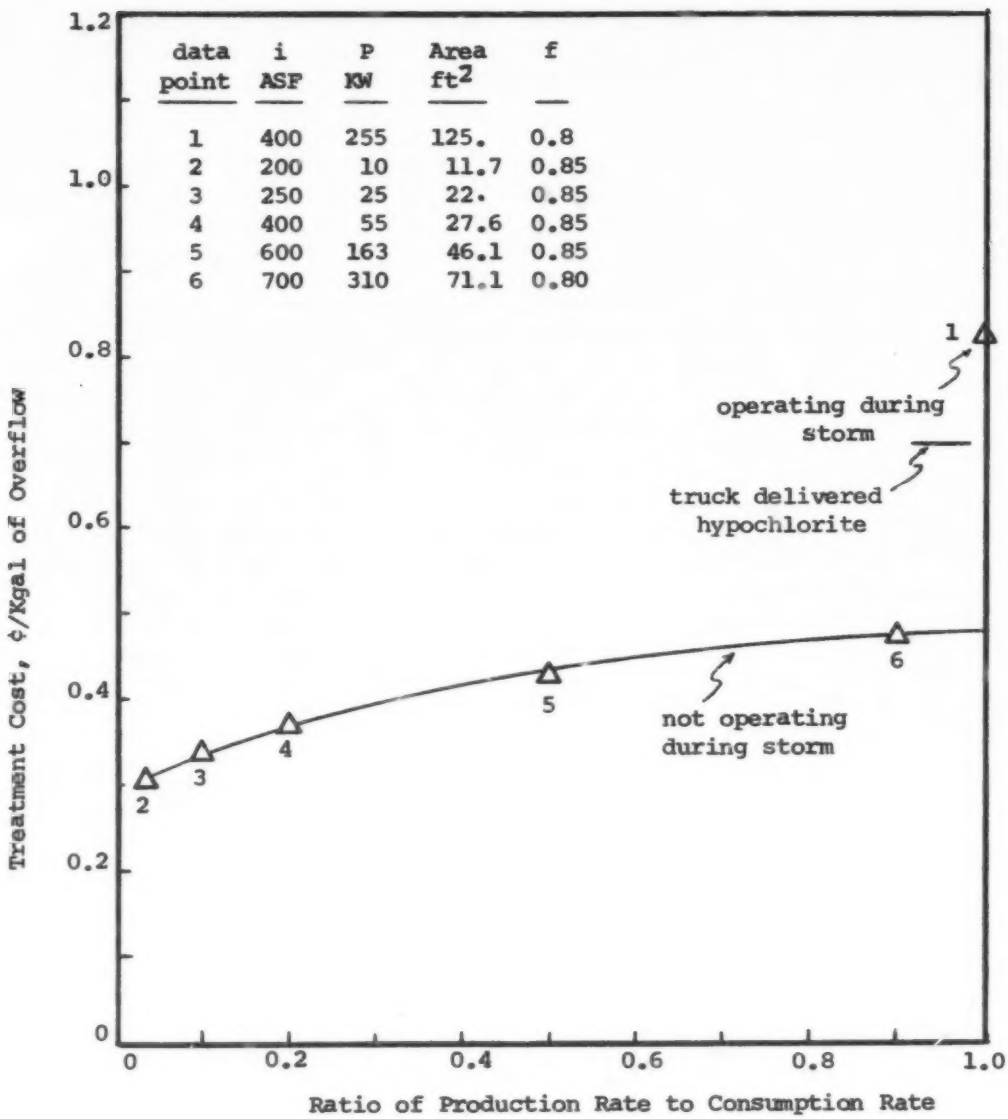
data point | i ASF | P KW | Area ft² | f
1 | 400 | 255 | 125. | 0.8
2 | 200 | 10 | 11.7 | 0.85
3 | 250 | 25 | 22. | 0.85
4 | 400 | 55 | 27.6 | 0.85
5 | 600 | 163 | 46.1 | 0.85
6 | 700 | 310 | 71.1 | 0.80
operating during storm
truck delivered hypochlorite
not operating during storm
Treatment Cost, ¢/Kgal of Overflow
Ratio of Production Rate to Consumption Rate
0
0.2
0.4
0.6
0.8
1.0
1.2

Figure 2d. Treatment Cost at the Boston University Bridge Facility

ACKNOWLEDGMENTS

Initial development of the hypochlorinator was performed under Program 11023 DAA of the Environmental Protection Agency, which was monitored by Allyn C. Richardson. The field unit was constructed under Grant 11023 DME to the Metropolitan District Commission under the supervision of Benjamin Fink, Director of Park Engineering and Chief Park Engineer. The opportunity to locate the hypochlorinator at the Boston University Bridge facility was kindly provided by Frank Burgin, Chief Engineer, Construction Division, M.D.C. The support and encouragement of William Rosenkranz of the Environmental Protection Agency throughout the project is especially appreciated.

SECTION V

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2. Ibl, N. and D. Landolt, J. Electrochem. Soc. 115, 713 (1968).

3. Foerster, F., Trans. Am. Electrochem. Soc., 46, 23 (1924).

4. Lewis, B.and G. von Elbe, "Combustion, Flame and Explosions of Gases," Academic Press, New York (1951).

5. Sconce, J. S., "Chlorine, Its Manufacture, Properties and Uses," Reinhold, New York (1962), p. 81 et. seq.

6. "Report on B.U. Bridge Storm Detention and Chlorination Station," C. A. Maguire and Associates, Boston, Mass. (1967).

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SECTION VI

PUBLICATIONS AND PATENTS

Michalek, S. A. and Leitz, F. B., "Cloromat - On-Site Generator of Hypochlorite," delivered at the 44th Annual Conference, Water Pollution Control Federation, San Francisco, California (1971).

Leitz, F. B., Accomazzo, M.A. and Michalek, S. A., "Development of Electrochemical Hypochlorite Generator," to be presented at the 141st National Meeting Electrochemical Society, Houston, Texas (1972).

No patentable items were developed on this contract.

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SECTION VII

GLOSSARY

Brine - A concentrated solution of salt. Here brine refers to a solution of sodium chloride at or near saturation.

Chlorine Equivalent - The amount of hypochlorite which would be required to perform the same oxidation as a given amount of chlorine.

Current Efficiency - The ratio of material produced to that which would be theoretically produced for a given current flow. The current efficiency for an overall process is the product of the efficiencies of the subordinate processes.

Endosmosis - The passage of water through a membrane caused by flow of current through that membrane.

Expanded Metal - A sheet of metal which has been slit and stretched to several times its original length. The resulting holes are roughly diamond shaped.

Internal Cell Resistance - The resistance to current flow presented by the electrolytic path between the electrodes. In practice it is convenient to use the slope of a plot of voltage versus current for internal cell resistance.

Ion Exchange Membrane - A sheet of plastic which has been chemically reacted to contain fixed sites of one charge. An electric current passed through this kind of membrane will be carried almost exclusively by species of the opposite charge.

Over-chlorination - The condition in a caustic-chlorine reactor caused by either local or general excess of chlorine over caustic.

Salt Utilization (Nominal) - The fraction of chloride fed to the anode compartment which would be converted to chlorine of the anode process were 100% efficient.

Salt Utilization (Real) - The fraction of chloride fed to the anode compartment which is converted to chlorine.

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SECTION VIII

APPENDICES

APPENDIX I. BOSTON UNIVERSITY BRIDGE FACILITY

Delays in construction of the Somerville Marginal Conduit have made initial testing at an alternative site desirable. The temporary site is to be the Boston University Bridge Storm Detention and Chlorination Facility (B.U. Bridge) in Cambridge, Massachusetts. This facility was designed to reverse the rapid degradation of the Charles River Basin (6). Its goal is to raise the basin to a water quality classification of "C", that is, suitable for boating and fishing.

The portion of this project of interest to the present paper is the provision for treatment of excess storm flow before disposal. During storms, flows in excess of 146 MGD are routed to the B.U. Bridge facility. There the mixed influent is screened and chlorinated with hypochlorite solution. The dosage rate which is expected to be between 2.7 and 3.5 ppm will be controlled to yield 1 ppm residual at the outlet of the tanks. Residence time in the tanks is 8 minutes at the design flow of 233 MGD. The treated effluent is discharged to the Charles River basin.

This facility was designed to use truck-delivered hypochlorite. It contains storage facilities for 8000 gallons. The estimated annual demand at this site is 50,000 lbs of chlorine equivalent per year which is 40% of the total design capacity of the field unit.

Results of the on-site tests will be reported by the E.P.A. upon completion of those tests.

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APPENDIX II. HYPOCHLORINATOR CELL FRAME AND FILTER PRESS DRAWINGS

Following are reductions of the drawings for the hypochlorinator cell frame and various drawings for the filter press which was specially designed to contain the electrochemical cell stack.

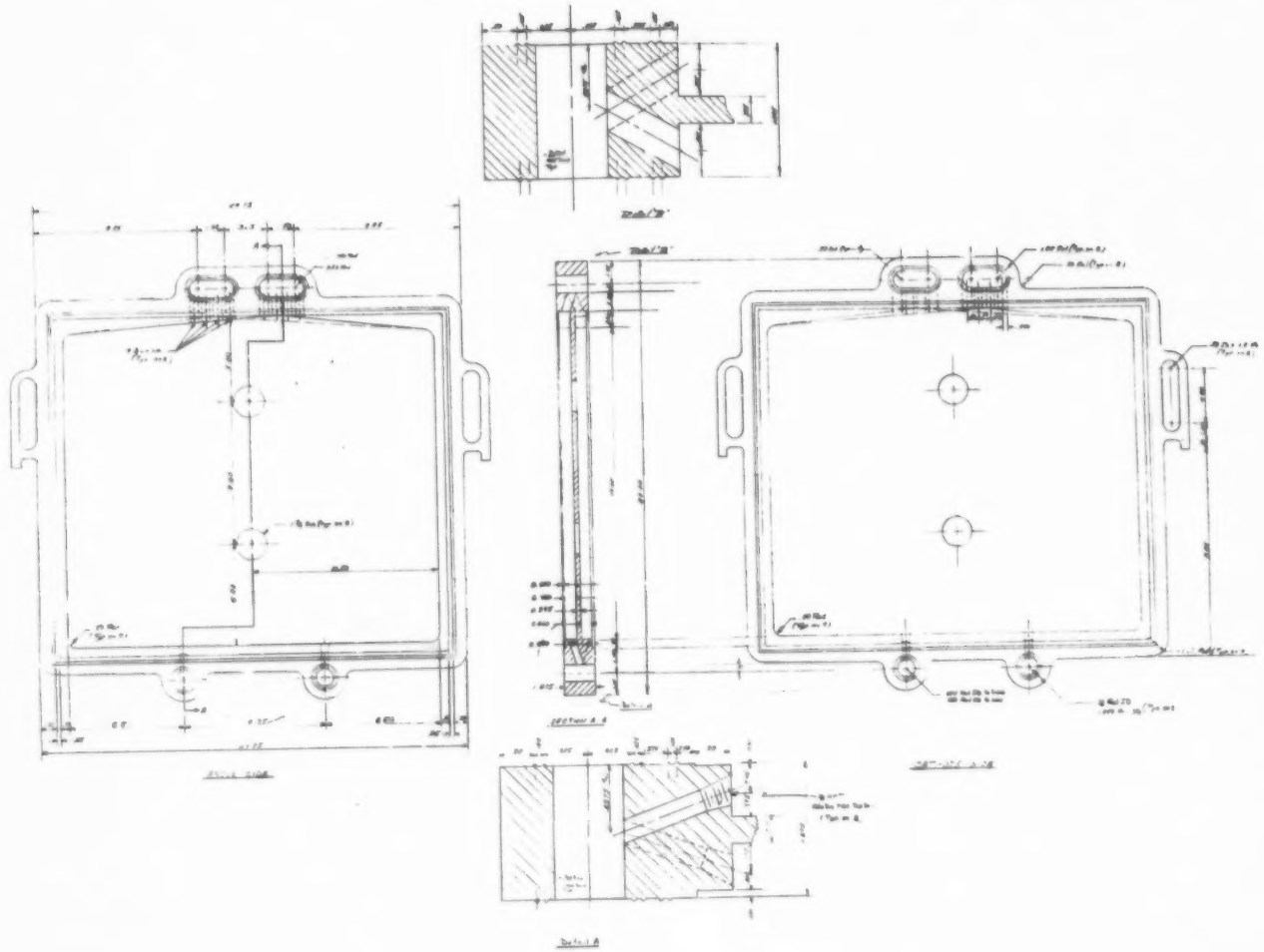

Figure 27. Hypochlorinator Cell Frame

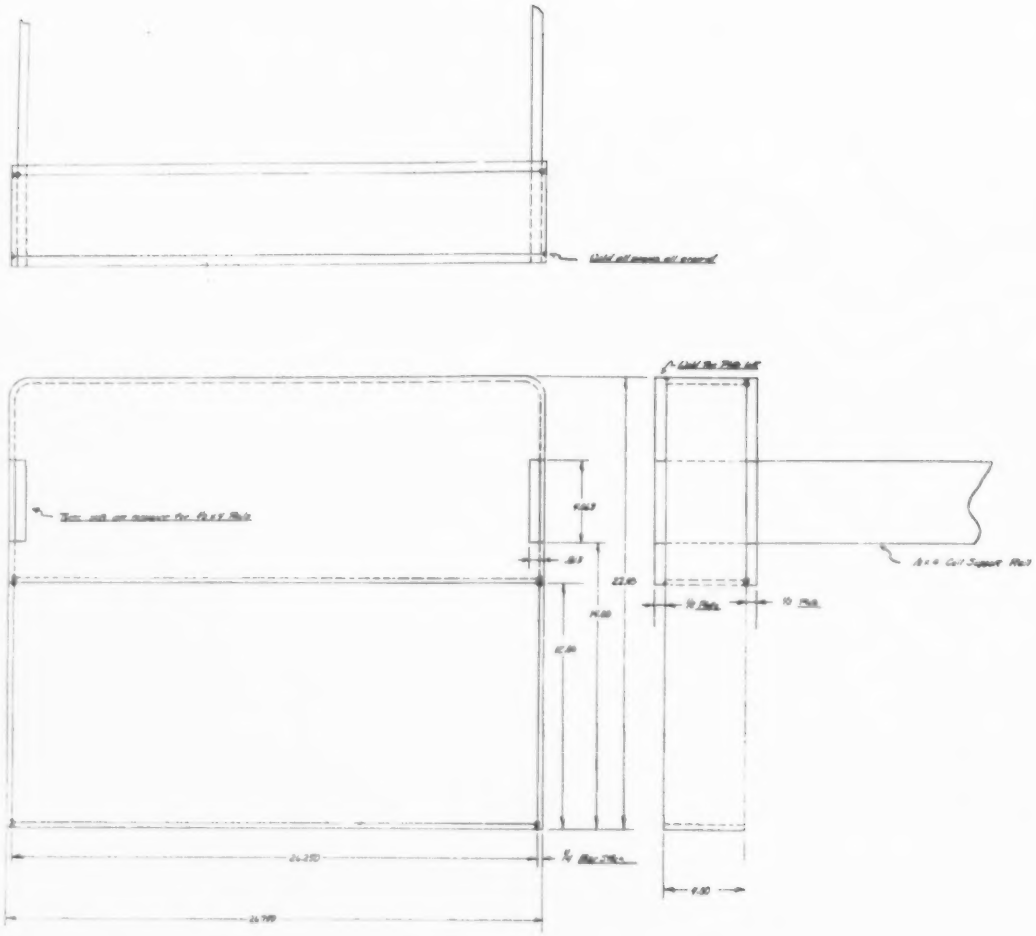

Figure 28. Cell Filter Press-Jack Support Frame (Drawing 5403-FP 203)

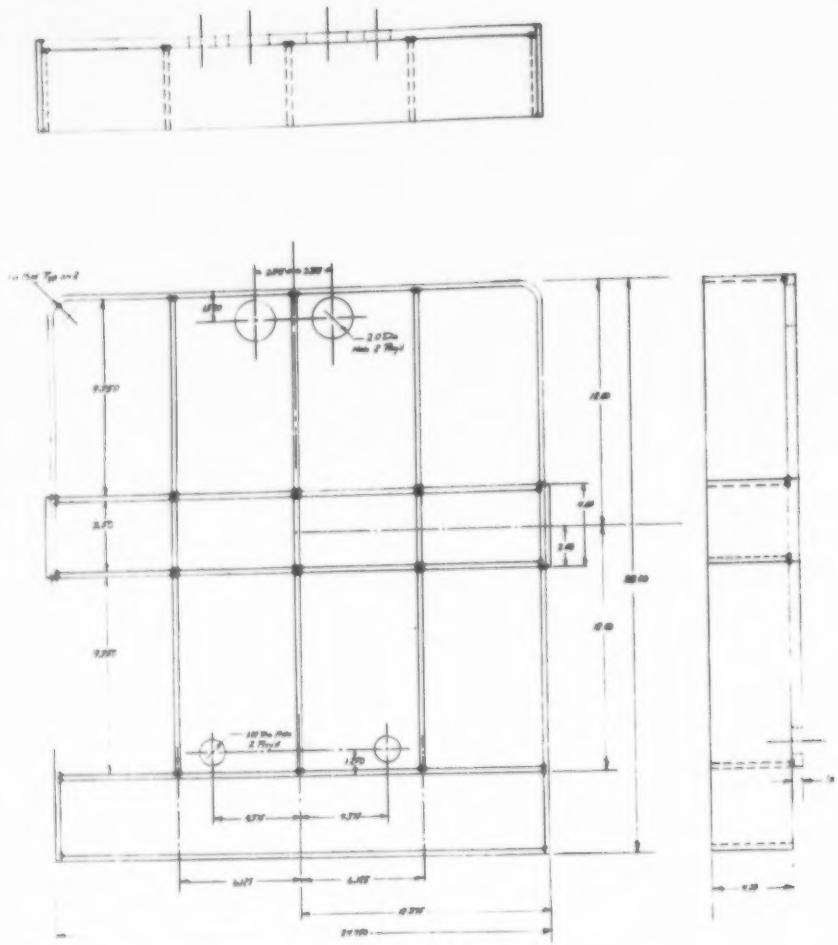

Figure 29. Cell Filter Press-Stationary Platen (Drawing 5403-FP202)

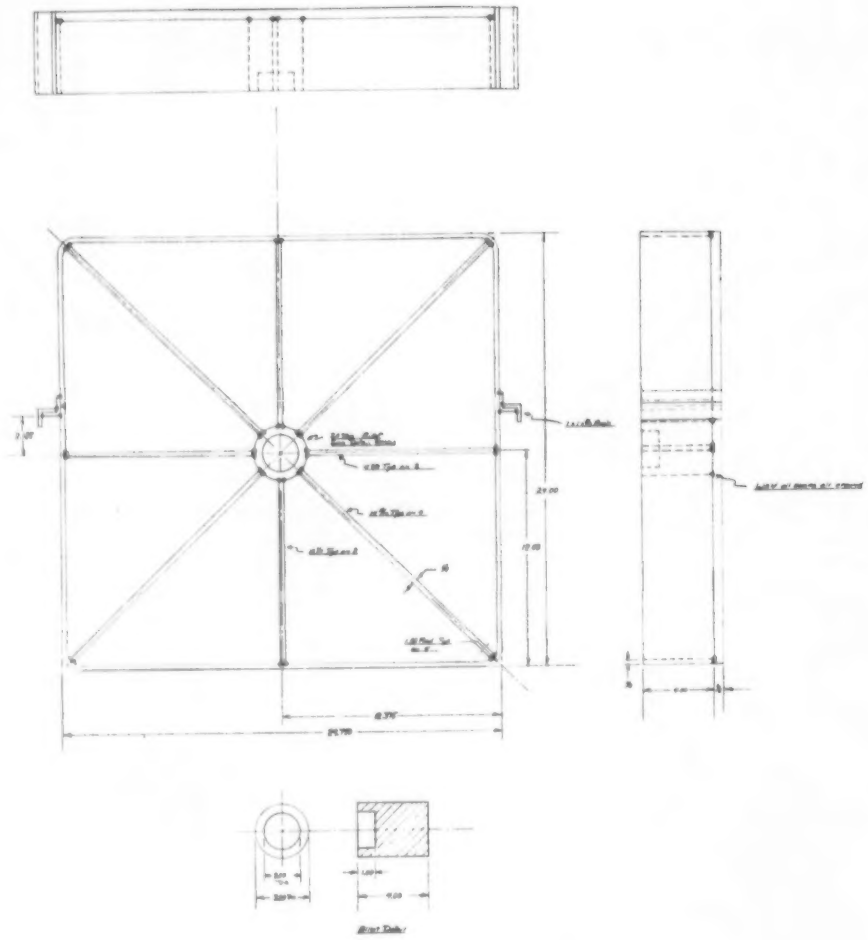

Figure 30. Cell Filter Press - Movable Plate (Drawing 5403-FP204)

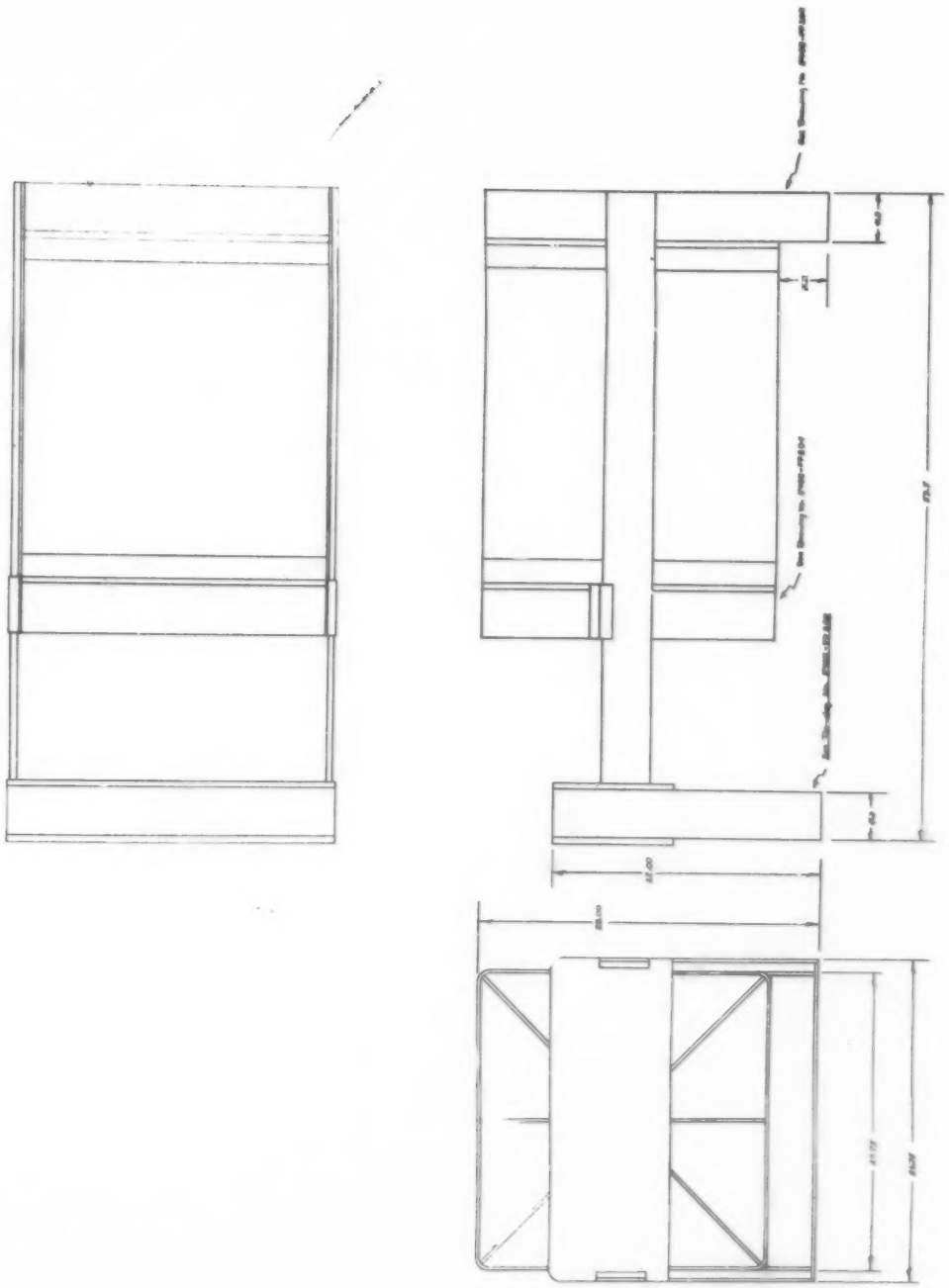

Figure 31. Cell Filter Press - Assembly Drawing (Drawing 5403-FP201)

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